PB-215 946

ADSORPTION FROM AQUEOUS SOLUTION

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Ann Arbor, Michigan

12 December 1966

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WP-00706

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THE UNIVERSITY OF MICHIGAN

COLLEGE OF ENGINEERING
DEPARTMENT OF CIVIL ENGINEERING

Progress Report

Adsorption from Aqueous Solution

WALTER J. WEBER, JR.

Supported by:

Department of Health, Education, and Welfare
Public Health Service
Grant No. WP-00706
Bethesda, Maryland

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Springfield VA 22151

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December 1966

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PROGRESS REPORT

Research Grant WP-00706

Adsorption from Aqueous Solution

Walter J. Weber, Jr.
The University of Michigan
Ann Arbor, Michigan

December 12, 1966

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1. Summary Page

Research Grant: WP-00706, Adsorption from Aqueous Solution

Principal Investigator: Walter J. Weber, Jr.

Sponsoring Institution: The University of Michigan
Dept. of Civil Engineering

Period of Report: January 1, 1964 - December 30, 1966

Date of Report: December 12, 1966

Summary Statement:

A number of different aspects of the adsorption of perdurable pollutants by carbon from aqueous solution have been studied to date. Primary emphasis has been directed toward provision of information for evaluation of the fluid-solid technique for treating waters and wastes. Pursuant to this objective the studies have included exploration of: a) flow rate, b) particle size, c) differences in adsorption patterns for different solutes, d) effects of solute concentration on uptake profiles and capacities of the columns, e) temperature effects on breakthrough and cumulative adsorption, f) pH effects on breakthrough and cumulative adsorption, and g) competitive effects on uptake profiles and adsorption capacities in two-component, three-component, four-component, and eight-component multi-solute systems. For all studies, initial attempts have been made to relate, qualitatively at least, column behavior to behavior in rapidly agitated non-flow systems in the hope that the more readily accomplished measurements on batch systems may be used ultimately for prediction of column behavior.

In addition to laboratory column studies, preliminary in-plant comparison have been made of fluid-carbon columns with

packed-carbon columns for treatment of effluent from a conventional activated-sludge treatment plant.

Studies related to the effects on adsorption of solute structure and molecular configuration, and of the nature of surface functional groups on active carbon have also been carried out. These studies have included a broad spectrum of organic pesticides of the thiophosphate, carbamate, dinitrophenol, and chlorophenoxy acid classes.

2. Detailed Report

(a) The research progress to date has been described in detail in four technical papers which have been prepared for publication in appropriate scientific journals. At the time of preparation of this report, each of these papers is either in press or under consideration for publication. Thus, as a detailed report of progress, the prepublication manuscripts of these four papers are submitted herewith.

(b) 1. "Fluid-Carbon Columns for Sorption of Persistent Organic Pollutants", W.J. Weber, Jr., Proceedings Third International Conference on Water Pollution Research, Munich, Germany, Sept. 5-6, 1966. (In press; prepublication manuscript attached hereto.)

2. "Mass Transfer Rates for Water and Waste Pollutants in Fluidized Adsorbers", W.J. Weber, Jr. and T.M. Keinath, Proceedings of Symposium on Research on Adsorption, AIChE, Detroit, Michigan, Dec. 8, 1966. (In press; prepublication manuscript attached hereto.)

3. "Sorption of Organic Pesticides from Aqueous Solution", W.J. Weber, Jr. and J.P. Gould, Advances in Chemistry Series, Symposium on Detection, Fate and Effects of Organic Pesticides in Environment, ACS. (In press; prepublication manuscript attached hereto.)

4. "Structure and Surface Chemistry of Active Carbon", V.L. Snoeyink and W.J. Weber, Jr. (Submitted to Journal Environmental Science and Technology for consideration; prepublication manuscript attached hereto.)

(c) Staffing: Professional Personnel

1. W.J. Weber, Jr., Ph.D., Principal Investigator, Assoc. Professor of Civil Engineering

   January 1, 1964 - present

   Approx. 20%

2. B.D. Kochhar, Ph.D., Post-Doctoral Research Fellow

   March 1, 1965 - March 31, 1966

   Full Time

Prepublication Manuscript

Not for Citation or General Distribution

FLUID-CARBON COLUMNS FOR SORPTION OF PERSISTENT ORGANIC POLLUTANTS*

Walter J. Weber, Jr.**

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* Paper presented at Third International Conference on Water Pollution Research, Munich, Germany, Sept. 5-6, 1966 (to be published in Conference Proceedings).

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The potential of adsorption as a method for achieving removal of persistent dissolved organic materials from polluted waters and waste waters is now well recognized, and considerable research interest has focused on the definition of parameters significant for the process and exploration of methods by which adsorption can be best utilized for waste water treatment.

Previous studies of adsorption on carbon in rapidly agitated non-flow systems have indicated that particle size of the adsorbent, among other variables, exerts a strong influence on rates of adsorption and adsorption capacities.(1,2) These findings suggest, as has been noted previously(3), that for practical application particle size should be as small as conditions of operation permit. The fluid-solid contact technique is one method by which fine particles of adsorbent may be used without introducing head losses of the magnitude normally associated with fine media in standard columnar operations. Further, problems of binding and fouling of fine media by entrapped air and particulate matter are minimal for the fluidized-bed method.

Heretofore, fluid-solid operation for improved contact in columns has attracted most interest for application to heat transfer(4,8), gas-solid mass transfer(4,7,9,10), and catalytic reactors.(4,11,12) Few reports have been given, however, of fluid-solid operations in which adsorption has been the primary function of the solid phase; even these few have been concerned primarily with adsorption from gas phase, and thus have little direct bearing on adsorption of organic substances from heterogeneous aqueous solutions.

Description of earlier phases of the present investigation of rates and capacities for adsorption of organic pollutants in fluid columns has been given previously.(3) In former studies factors of flow rate, particle size, and nature of the adsorbent were investigated for single-solute solutions. The present research extends the previous work to more complex, multiple-solute systems for investigation of competitive interactions between solutes and provision of information for evaluation of the fluid-solid technique for treating wastes containing various types of organic substances. Pursuant to these objectives, the studies include exploration of: a) possible differences in adsorption patterns for different solutes; b) effects of solute concentration on adsorption uptake profiles and capacities of the columns; c) temperature effects on breakthrough and cumulative adsorption; d) pH effects on breakthrough and cumulative adsorption; and, e) competitive effects on uptake profiles and adsorption capacities in two-component, three-component, four-component, and eight-component multiple-solute systems. For all studies, attempts have been made to relate, qualitatively at least, column behavior to behavior in rapidly agitated non-flow systems in the hope that the more readily accomplished measurements on batch systems may be used ultimately for prediction of column behavior.

In addition to laboratory studies, preliminary in-plant comparisons have been made of fluid-carbon columns with packed-carbon columns for treatment of effluent from a conventional activated-sludge treatment plant.

I. LABORATORY INVESTIGATIONS

DETAILS OF EXPERIMENTAL TECHNIQUES

For the laboratory studies, the columns consisted of Lucite tubes, approximately 1 meter in length and 2.54 cm in diameter, fitted at the bottom with a velocity-head dissipation chamber filled with 2-mm glass beads. For most studies the columns were packed with 45 grams of carefully sieved and washed carbon, yielding a settled depth of approximately 22 cm. Larger quantities of carbon and longer columns were used for some studies. Flow to the column from a constant-head tank was regulated by means of needle-valve controls. Effluent from the column passed through an air-gap to prevent siphoning and pressure fluctuations, through a 1-liter settling basin to remove fine materials carried over in the effluent, and into one of several volume-calibrated collection reservoirs. In addition to "instantaneous" samples taken at the top of the column and at selected ports along its length for analysis of residual concentration, samples of the total effluent were analyzed at appropriate intervals to provide a check on the cumulative quantity of solute adsorbed on the column of carbon.

Organic solutes have been selected for the laboratory studies largely on the basis of their occurrence and persistence in wastes and polluted waters. Ultrawet K, a branched-chain sulfonated alkylbenzene obtained as a 93-%-active-material sodium salt from the Atlantic Refining Company, has been the most commonly used solute The average molecular weight of the Ultrawet K based on its ultraviolet absorbance, using a molar absorptivity of 12.9 x 10^6 cm^2/mol at 225 mμ for sulfonated alkylbenzenes(13), has been found to be 396 grams. Substances obtained from the Dow Chemical Company for the studies include: nonylphenoxypolyethoxyethanol (a nonionic surfactant), 2-sec-butyl-4,6-dinitrophenol (a herbicide-insecticide), phenyl-N,N-dimethylphosphorodiamidate (an insecticide), and 2,4-dichlorophenoxyacetic acid (a herbicide). Sodium dodecylsulfate, a Matheson, Coleman and Bell product, was better than 95% pure in dodecylsulfate and 99.5% in total alkylsulfate by analysis. Triethanolamine, quinine sulfate, phenol, 2,4-dichlorophenol, and sodium p-toluenesulfonate were obtained as reagent grade products from Eastman Organic Chemicals.

Ultraviolet absorption(13) has been used for determination of the concentration of the sulfonated alkylbenzene, Ultrawet K, in experiments in which this solute has been the only adsorbate present in solution. When this substance has been a component of solutions in which other solutes cause interference with the ultraviolet method, the Longwell and Maniece modification of the Jones method using methylene blue has been employed.(14) Ultraviolet absorption has been used for determination of p-toluenesulfonate.(13)

It has been possible also to determine readily the concentrations of many of the other substances by light absorption in the visible or ultra-violet region. Quinine exhibits a maximum in light absorption at 330 mμ with a molar absorptivity of 4.70 x 10^6 cm^2/mol; 2,4-dichlorophenol has a maximum in absorption at 284 mμ with a molar absorptivity of 2.05 x 10^6 cm^2/mol; and 2-sec-butyl-4,6-dinitrophenol (DNOSBP) has a maximum at

375 mμ with a molar absorptivity of 13.80 x 10^6 cm^2/mol. The absorption of each of these substances has been found to follow the Beer-Lambert law for the range of concentrations studied. Thus measurements of absorbance at the indicated wave-lengths permit rapid and accurate determination of the corresponding substances.

The remaining solutes have been used solely as components of complex mixtures of organic compounds, and determinations of their individual concentrations have not been made. Rather, effectiveness of adsorption in experiments with complex mixtures has been evaluated in terms of the over-all removal of organic pollutants, measured in terms of total organic carbon. Determinations of organic carbon have been made according to a high-temperature wet oxidation technique.(15)

A coconut-based active carbon, Columbia LC grade obtained from the National Carbon Company, has served as the adsorbent for the majority of the laboratory studies. A coal-base carbon, grade SGL from the Pittsburgh Activated Carbon Company, also has been employed for a number of laboratory investigations.

Prior to use each adsorbent was separated by thorough sieving into uniform particle sizes; then portions of suitable size-range were washed in distilled water to remove leachable impurities and adherent powder and were next dried at 105°C. The size chosen for most extensive study comprised particles passing a United States Standard Sieve No. 50 and retained on a No. 60 sieve; the mean particle diameter for this size range is 0.273 mm.

When not otherwise specified in the text, a 45-gram quantity of 0.273-mm Columbia LC carbon has been employed as the adsorbent charge for a column study, and the flow rate has been 2.5 gallons per minute per square foot (102 l/min/sq.m).

RESULTS

Solute Effects

i) Type of Solute - Previous experiments on adsorption by carbon in fluidized columns have been conducted with highly-branched sulfonated alkylbenzenes.(3) It has been of interest in the present work then to explore possible differences in adsorption patterns for different solutes upon passage through fluid-carbon columns and to ascertain whether observed differences can be correlated with characteristics found through more readily accomplished measurements on agitated non-flow systems. Hence, in one experiment parallel columns have been run with two solutes having considerably different molecular weights but of the same chemical class of compound, namely Ultrawet K and sodium p-toluenesulfonate. The latter is the simplest sulfonated alkylbenzene, with a molecular weight of 171 for the anion; the former is a branched-chain sulfonated alkylbenzene with about 15 carbon atoms in the alkyl group.

The choice of these particular solutes has been based on the fact that rates and capacities for adsorption on active carbon from solution have been studied previously for p-toluenesulfonate and for materials very similar to the Ultrawet K in batch-type systems, and marked differences in their adsorption characteristics have been observed.(1,2)

Figure 1 presents a comparison of data for the adsorption of Ultrawet K from a 73.3-μM solution with data for adsorption of p-toluenesulfonate from a 79.6-μM solution. The form of the curve representing the relative effluent concentration, C/C_0, as a function of time for the Ultrawet K is quite similar to that obtained previously for other highly-branched sulfonated alkylbenzenes under similar experimental conditions.(3)

Several points of comparison should be noted in Figure 1. First, there is evidence of an initial leakage of p-toluenesulfonate considerably greater than that for the branched-chain material, the leakage of the p-toluenesulfonate being 6% of its influent concentration to about 2% for the latter. Second, the effluent leakage for the p-toluenesulfonate increased very little for the first twenty hours of operation whereas that for the high-molecular-weight compound increased almost from the start and after sixteen hours of operation became greater than the leakage from the p-toluenesulfonate column. Third, as a corollary to the second point, the total break-through of p-toluenesulfonate was much sharper than that of the Ultrawet K. After about sixty hours the uptake of Ultrawet K from solution was once again more effective than uptake of the p-toluenesulfonate. Fourth, after about 100 hours the total integrated uptake from each of the two solutions was about the same, but about one-third of the influent branched-chain material was still being removed whereas the capacity for adsorption of p-toluenesulfonate had apparently been exhausted.

The fact that the Ultrawet K is taken up more completely during the very early stages of the run than is the p-toluenesulfonate is in accord with findings of previous equilibrium studies in batch systems. During the first few hours of the experiments the concentration of each solute in the water passing up through the expanded bed of fresh carbon is reduced to a low figure beyond the first few inches of the column. Previous investigations of the equilibria of adsorption on carbon have indicated that the energy of adsorption for a high-molecular-weight sulfonated alkylbenzene is greater than for p-toluenesulfonate.(2) That is, effective adsorption is observed for much smaller concentrations with the former than with p-toluenesulfonate. Thus, removal by adsorption of the last traces of the high-molecular-weight Ultrawet K should be considerably easier than complete cleanup of the p-toluenesulfonate.

The increasing leakage of the Ultrawet K in contrast to that of the p-toluenesulfonate over the first 20 hours of column operation can be associated with the relative rates of adsorption observed in batch studies on these solutes.(1) Because of the slow rate of penetration of the larger molecule into the interior of the carbon granules the active external points soon reach a significant fraction of saturation and subsequent adsorption is less rapidly effective. With the p-toluenesulfonate a relatively rapid migration of adsorbed material to the interior permits renewal of active external surface and substantial maintenance of efficiency of adsorption for a longer period. When nearly full capacity has been attained, there is a relatively sharp break-through.

Maintenance of adsorption capacity in the column adsorbing Ultrawet K beyond the time required to exhaust the column adsorbing p-toluenesulfonate is expected on the basis of the greater adsorption capacity for the former material found in the batch equilibrium studies.(2)

The separate column studies with Ultrawet K and p-toluenesulfonate thus give indication that at least qualitative prediction of column behavior may be possible from knowledge of batch-system behavior, at least for cases in which a single-solute solution is passed through the column.

ii) Concentration of Solute - Figure 2 presents break-through curves for three experiments in which the effects of different concentrations of Ultrawet K have been studied. The effect of concentration on break-through of solute is as would be expected, that is, the higher the concentration the more rapid the break-through. Yet it may be noted that at the points corresponding to $C/C_o = 0.1$ the total weights of solute adsorbed were about the same in all three runs

Although leakage appears greater at the smaller influent concentrations, it should be noted that the actual effluent concentrations at zero time were 0.85, 1.5 and 0.8 ppm for increasing influent concentrations. It thus appears that initial effluent concentrations will be determined primarily by the depth of the adsorption column rather than by the influent concentration.

One other noteworthy point is that with the lowest influent concentration, 13.2 μmol/l or 5.2 mg/l, better than 90% adsorption was maintained with just a 22-cm settled depth of carbon for more than 5 days This would mean about 40 days effective operation for a five-foot settled depth with this concentration of material to be removed.

Figure 3 shows total quantity of solute removed from solution by the 45 grams of carbon in each experiment. As would be expected on the basis of the increased driving force for transfer with increased concentration of solute in solution(3), and the greater capacity of the carbon at the greater influent concentration, both the rate of uptake and total quantity of solute removed is greater at the higher influent concentrations of Ultrawet K for the same period of time. After 100 hours of operation, the carbon in the experiment in which the influent concentration of solute was 73.3 μmol per liter had removed a total quantity of solute equal to approximately 11% of the weight of the adsorbent, and for the experiment with C_o = 13.2 μmol per liter the solute removed was about only 3% of the weight of the carbon. Since it was impractical to carry on the experiments at the lower initial concentrations until the carbon was exhausted full capacities as a function of concentration could not be measured.

Temperature Effects

Three experiments have been carried out with Ultrawet K as solute at solution temperatures of 36°C, 28°C, and 16°C. The initial concentrations of solute were closely the same, in the range of 77-80 μmols per liter. The experiment at 28°C was at room temperature; for the experiment at 16°C the influent was chilled by means of a conventional Freon compressor with the cooling coil immersed in the constant-head tank; a blade-type heater was used in the constant-head tank to heat the influent for the experiment at 36°C. Each temperature given is an average of the temperatures of the influent and effluent for a column. Temperature differences between the influent and effluent for each experiment were less than 3°C.

Little difference in the total uptake of solute as a function of time in the fluid-carbon columns has been observed for any of the temperatures studied. Such a result is to be expected, for total uptake is primarily a function of adsorptive capacity of the carbon with beds of sufficient depth, and depends very little on the rate of adsorption. Adsorptive capacity has been shown not to change greatly over a small temperature range such as that used in these experiments.(2) Temperature effects should be noted most significantly for column work in the steepness of the breakthrough portion of the curve of relative effluent concentration as a function of time. At lower temperatures, where rate of adsorption is low, increasing leakage should begin sooner and a more gradual approach to full saturation should be observed. Only a very slight indication of increased leakage for the experiment at 18°C over those at 28°C and 36°C was given in the present experiments.

Effect of pH

Preliminary information on the effect of solution pH on uptake in a fluid-carbon column has been obtained by passing a solution of sulfonated alkylbenzene, with an unadjusted pH slightly below neutral, through a column containing 45 grams of 0.359-mm Columbia LC carbon. The larger particle size was used to permit more rapid break-through for the preliminary study. When the value of C/C_o for the experiment reached 0.55, the pH of the influent was decreased to 2.5 by addition of concentrated phosphoric acid. As illustrated in Figure 4, the decrease in leakage after acidification of the influent is dramatic.

To test the effect of solution pH more extensively, four additional experiments have been conducted at different pH values, each with a column containing 45 grams of 0.273-mm Columbia LC carbon. The initial concentration of sulfonated alkylbenzene in each experiment was within the range from 79 to 81 μmol per liter. Adjustment of pH in the solutions to values of 3.9, 6.6, 7.9, and 10.0, respectively, was accomplished with phosphoric acid-phosphate buffer systems. The pH values given are for influents to the columns.

Data for the pH studies are presented in Figure 5, which shows the total quantities of solute removed from solution by the carbon as a function of time. There is a notable difference between the total amounts of solute removed from solution in the experiments at the highest and lowest pH values tested, the total amount at any time being considerably greater at low pH. The experiments at intermediate pH levels are observed to fit the pattern of increasing removal with decreasing pH. The observed dependence of solute removal on pH for the column studies accords with previous work in which both rates and final positions of equilibrium for adsorption of sulfonated alkylbenzenes on the experimental carbon in batch-type systems were found to increase with decreasing pH.(1,2)

Even so, in order to show marked changes in adsorption with pH it has been necessary to go to very high or low pH values. Over the pH range of particular interest, 6 to 8, differences in adsorption efficiency appear to be minor. More pronounced effects may be obtained with other types of pollutants, but in general it can be expected that normal pH variations will not affect significantly the operation of active-carbon columns.

Multiple-Component Solutions

That solutes in multiple-component solutions compete with one another for adsorption on carbon has been demonstrated for agitated non-flow systems.(16) Studies have been carried out during the present investigation to explore the nature and extent of competitive interactions in continuous flow systems. Such studies are significant for evaluation of the suitability of continuous-flow adsorption systems for waste-water treatment, for rarely does the waste water to be treated contain but one organic pollutant. Rather, waste waters are likely to be heterogeneous mixtures of complex organic substances of different chemical types or classes.

In these investigations, solute mixtures of two, three, four, and eight components have been studied.

i) Two-Solute Systems - Some pronounced effects of sodium dodecylsulfate on the adsorption of sulfonated alkylbenzenes in non-flow systems have been noted previously.(16) Hence, mixtures of sodium dodecylsulfate and the branched sulfonated alkylbenzene, Ultrawet K, have been employed as solutes in initial studies of adsorptive competition in fluid-carbon columns.

The mixed solution for this study was comprised of 71.6 μmol per liter of Ultrawet K and 75.0 μmol per liter of dodecylsulfate. Because a simple analytical technique for dodecylsulfate in dilute solution is not available, only the concentration of the sulfonated alkylbenzene was determined in the effluent. For purposes of comparison a separate experiment with a pure solution of the Ultrawet K in a concentration of 73.3 μmol per liter was carried out under identical conditons.

It was immediately apparent from this study with a relatively simple two-component solution that the presence of the dodecylsulfate has a marked effect on the over-all adsorption of the sulfonated alkylbenzene. However, the competitive effect appeared to be not significant in the early stages of the run; a major difference between break-through curves for Ultrawet K in mixed and pure solution was noted only after about 55 hours ($C/C_o \sim 0.5$) of operation of the columns. During the first 55 hours the carbon apparently had sufficient capacity for both solutes so that little effective competition for adsorption occurred. Since in this experiment the dodecylsulfate was added to the sulfonated alkylbenzene concentration rather than replacing part of it, any quantity of the former adsorbed would be expected eventually to reduce the adsorptive capacity for the latter.

ii) Three-Solute Systems - To test further the effects of solute interactions on adsorption in fluidized columns from solutions containing mixtures of organic compounds, a column study has been run with a solution containing three different classes of organic compounds. The influent solution consisted of Ultrawet K at a concentration of 43.6 μmol per liter, 2-sec-butyl-4,6-dinitrophenol (DNOSBP) at a concentration of 31.8 μmol per liter, and quinine sulfate at a concentration of 26.9 μmol per liter (as the quinine base).

Analyses for concentration of the Ultrawet K in the mixed solution were carried out with the methylene blue procedure mentioned previously(14); no interference from the quinine or the DNOSBP was experienced with this procedure. Determinations of quinine and DNOSBP were made by spectrophotometric measurements at 330 mμ and 375 mμ, respectively. The molar absorptivities for these substances at their respective wave lengths for peak absorption have been listed previously in this paper. At 375 mμ the molar absorptivity of the quinine was 0.07 x 10^6 cm^2/mol, and that for the DNOSBP at 330 mμ was 4.71 x 10^6 cm^2/mol. Determinations of individual concentrations of these two solutes thus required measurement of each sample at each of the two wavelengths, and simultaneous solution of two absorbance-concentration equations.

Figure 6 shows break-through curves for each of the components of the mixture. The break-through for the sulfonated alkylbenzene (ABS) in the mixture is much more rapid than is that for a pure solution of similar initial concentration. This fact is illustrated by the curves plotted in Figure 7. The break-through curve shown in Figure 7 for the single-solute solution has been obtained under identical flow and adsorbent conditions with a 39.4 μmol per liter solution of the Ultrawet K.

On the other hand the break-through is not as rapid as would have been expected for the sulfonated alkylbenzene alone at a concentration equal to 102 μmol per liter, the sum of the component concentrations. In fact the curve is rather similar to that obtained with 73 μmol per liter of Ultrawet K. This tends to indicate some enhancement of total adsorptive capacity for the mixed components, in accord with the findings of previous studies of competitive adsorption in non-flow systems.(16)

There were no single-solute column studies for quinine and DNOSBP with which the other curves in Figure 6 might be compared.

The curves shown in Figure 6 do not bring out completely the adsorption picture for this experiment with a multi-component solution. Figure 6 alone gives the impression that the amount of sulfonated alkylbenzene adsorbed was less than the amount of DNOSBP adsorbed, and that the amount of quinine adsorbed was greatest of all. Actually, because of the initial differences in concentration the amounts of individual solutes removed from the mixed solution flowing through the column were the reverse of this order. This is shown by the cumulative uptake plots in Figure 8.

Comparison of Figure 8 with Figure 3 shows that the extent of adsorption of the sulfonated alkylbenzene from the mixture was less than that from a pure solution of approximately the same concentration for long periods of operation. For example, the quantity of this material adsorbed from the mixture after 100 hours was about 130μ mols per gram of carbon, while for a pure solution of similar initial concentration the quantity adsorbed after 100 hours was about 210μ mols per gram of carbon (Figure 3). However the total organic matter adsorbed after 100 hours - the sum of ABS, DNOSBP and quinine was 350μ mol/gram.

In an effort to determine whether the observed adsorption patterns for the mixture could be predicted from batch-system studies, kinetic and equilibrium experiments with non-flow systems have been conducted using the same mixture of the three solutes and also with solutions of the three individual components in each of which the initial concentration of solute was the same as its initial concentration in the mixture. Summary data for these experiments are presented in Table 1.

Values for the relative rate constant, k, in Table 1 have been derived from normalization of the rate data by plotting amount removed from solution as a function of the square root of the time, according to an intraparticle-transport rate mechanism (1,17). The parameter, k, represents the square of the slope of the resulting linear plot. These data indicate that the rate of adsorption of DNOSBP is by far the most adversely affected in the mixture. There seems to be some tendency for all the rates to reduce to a more nearly common value in the multiple-component solution. This is also indicated by the parallel slopes of the break-through curves in Figure 6.

TABLE 1

Relative Rates of Adsorption from Single- and Multiple-Solute Systems*

	Relative Rate Constant, k, [$(\mu mol/g)^2/hr$] x 10^{-3}	
Solute	Single-Solute Solution	Multiple-Solute Solution**
sulfonated alkylbenzene	3.60	1.85
quinine	7.23	1.60
2-*sec*-butyl-4,6-dinitrophenol	57.60	0.26

* 0.273-mm Columbia Carbon, Agitated Non-Flow System, 28°C

**Mixture: 43.6 μmol/l sulfonated alkylbenzene;
26.9 μmol/l quinine;
31.8 μmol/l 2-*sec*-butyl-4,6-dinitrophenol

Isothermal equilibrium studies at 30°C for the individual component solutions were also conducted using 0.273-mm Columbia carbon. Langmuir adsorption constants for all three solutes are listed in Table 2; X is the amount of adsorbed material per gram of carbon, X_m is the limiting value of X for monolayer adsorption according to the Langmuir model, C is the concentration of solute in solution at equilibrium, and b is a constant expressive of the energy of adsorption and equal to the reciprocal of the concentration at which adsorption is equal to $X_m/2$.

TABLE 2

Langmuir Constants for Adsorption Isotherms*

Langmuir equation: $X = X_m bC/(1+bC)$

Solute	X_m, $\frac{C_o - C_{eq}}{m}$, $\frac{\mu mol}{g}$	b, $\frac{1}{\mu mol}$
sulfonated alkylbenzene	455	0.478
quinine	605	4.13
2-**sec**-butyl-4,6-dinitrophenol	1,850	0.174

*0.273-mm Columbia Carbon, 30°C

Attempted correlation of these batch studies with the previous column studies is difficult and probably premature, for neither the batch nor the column studies have been sufficiently complete. The only direct comparison to be made between the batch studies on the rates of adsorption and the continuous-flow studies is with the slopes of the breakthrough curves for the columns. Unfortunately the slopes of the breakthrough curves with the shallow beds used in these studies have not been well enough defined to make such a comparison completely meaningful. Conversely, the relative amounts of uptake for the individual solutes in the mixture might be compared with data on individual adsorption isotherms in the multi-component solution, but these latter data have not yet been obtained.

It is tempting to relate the great reduction of rate of uptake of DNOSBP in the multi-component solution as compared with pure solution with the comparatively low "b" value obtained in the isotherm studies and with the reduced capacity for adsorption shown in the mixed-column studies. Yet, it must be admitted that fitting of the Langmuir equation to the equilibrium adsorption data for a substance like DNOSBP that exhibits an apparent X_m value equal to better than 40% of the weight of carbon is questionable from a theoretical point of view, since the monolayer assumption is almost certainly invalid.

For the present, then, these results must simply be added to the fundamental data on adsorptive behavior being accumulated for later use when more complete delineation of the systems has been accomplished.

iii) Four-Solute Systems - Another column study has been conducted with a solution containing four different classes of organic compounds, both to determine the adsorptive patterns of some other types of solutes in multiple-component solutions and to investigate break-through effects in deeper columns of a carbon more suitable for practical use in waste-water treatment.

A multiple-component solution containing 24.5 mg/l Ultrawet K (ABS), 15.5 mg/l triethanolamine (TEA), 16.9 mg/l 2,4-dichlorophenol (2,4-DCP), and 53.7 mg/l nonylphenoxypolyethoxyethanol (9N10) was passed upward through a one-inch column containing 200 grams of 0.273-mm Pittsburgh SGL carbon, at a rate of 2.5 gpm/ft^2 (102 l/min/sq.m). The expanded height of the carbon column was 209 cm. In addition to routine determinations for concentrations of total organic carbon, sulfonated alkylbenzene and 2,4-dichlorophenol in the effluent from the column, several 20-liter samples of the effluent were concentrated by vacuum distillation and analyzed by infrared spectrophotometry.

Figure 9 is a plot of data for the uptake of organic material by the Pittsburgh carbon during this 180 hour experiment. The data have been plotted in terms of organic carbon removed from solution as a function of time. It has been possible, as illustrated in Figure 9, to account for the fractions of organic carbon existing respectively as sulfonated alkylbenzene and 2,4-dichlorophenol because these materials were determined individually. Although one fraction is represented as being composed of triethanolamine plus nonylphenoxypolyethoxyethanol, infrared analyses showed complete uptake of 9N10 and considerable leakage of triethanolamine.

After about 150 hours of operation it became difficult to maintain the flow-rate of 2.5 gpm/ft^2 (102 l/min/sq.m) with the available head of 10 ft (3.05 m) because of increased density of the carbon and clogging of the material in the column. At 180 hours it became impossible to hold the rate with the experimental apparatus and the run was terminated.

After 180 hours the C/C_o value for total organic carbon in the effluent had reached a value of only about

0.2. No significant concentrations of sulfonated alkylbenzene or 2,4-dichlorophenol were found in the effluent up to this point by standard determinations. The periodic infrared analyses of concentrated effluent indicated that the only material being carried over in the effluent in any significant amount was the triethanolamine; approximately 50% of this material was passing completely through the column.

If the weight of the organic carbon in the mixture of organic solutes is taken as one-half the total weight of organic material, then as shown by Figure 9 the total amount of organic material removed from solution by the Pittsburgh carbon during the 180 hour run was about 400 mg per gram or a very high capacity of 40%-by-weight for the carbon to this point. To check this, a mass balance was run by removing the carbon from the column and drying it in a very thin layer at 105°C for 24 hours. The carbon was weighed after drying and found to weigh 279.5 grams. Thus the mass valance gave good confirmation of high capacity of 40%-by-weight. The results of this experiment indicate that good capacities with resulting economy in cost of carbon may be realized for some pollutants.

On the other hand, the early breakthrough of triethanolamine shows that some selectivity in removal of pollutants will be observed in practice and give some indication of the types of compounds that may not be effectively removed by carbon.

iv) Eight-Solute Systems - One column study was run with a very complex mixture of assorted classes of organic solutes. The solutes comprising the mixture, along with their respective concentrations in the influent, are listed in Table 3.

TABLE 3

Composition of Eight-Component Solute Mixture

Solute	Concentration in Influent, mg/l
phenol	2.4
quinine	9.3
dodecylsulfate	7.2
sulfonated alkylbenzene	10.6
2-*sec*-butyl 1-4,6-dinitrophenol	6.0
2,4-dichlorophenoxyacetic acid	5.5
nonylphenoxypolyethoxyethanol	16.5
phenyl N,N'-dimethylphosphorodiamidate	5.0

The column used in this experiment contained 100 grams of 0.273-mm Pittsburgh carbon, and the flow rate was 2.5 gpm/ft^2 (102 l/min/sq.m). Total organic carbon was the only analytical measure used to determine the effectiveness of the column.

Continuous flow was maintained for approximately 100 hours; then experimental difficulties forced termination of the experiment - for some reason prolific microbiological growth developed in the influent solution, presumably made up largely of resistant substrates. At the forced termination of the run the value of C/C_o for total organic carbon had reached a level of only about 0.1, and the total quantity of organic carbon removed from solution up to the time of termination was 8.5 grams. Thus the capacity attained by the adsorbent, up to the point when the experiment was stopped, was on the order of 15% on the assumption that the weight of organic matter was twice the organic carbon. Indication is then that again very high capacity would have been attained prior to that time at which the effluent concentration reached an undesirably high level.

II. IN-PLANT INVESTIGATIONS

DETAILS OF EXPERIMENTAL TECHNIQUES

Preliminary work has been initiated on the extension of the laboratory experiments with fluid-carbon columns to in-plant investigations. The in-plant studies are being made at the Ypsilanti, Michigan, Sewage Treatment Plant. The Ypsilanti plant employs conventional activated sludge treatment, and the present adsorption studies have been on the final effluent from this plant.

The primary purpose of these initial in-plant studies has been to compare, under practical conditions, the effectiveness of the fluid-column method of operation with that of the conventional packed-column method for advanced treatment of waste waters.

The experimental apparatus is illustrated schematically in Figure 10. Column No. 1 in Figure 10, a Lucite tube 5.1 cm in diameter and 3.66 meters in length, has been employed for fluid-column operation and Column No. 2, half as long as the first column but otherwise identical, has been used for packed-column operation. In both instances flow is from the bottom to the top of the column. The columns are each provided with velocity-head dissipation chambers at the bottom or influent end, in a fashion similar to the columns used in the laboratory studies. Stainless steel screens separate the carbon from the glass beads in the dissipation chamber and a similar screen is provided at the top of the packed column. For the experiments, each column has been charged with 2000 grams of 0.503-mm Pittsburgh SGL carbon.

For maintenance of constant flow rate, sigmoid pumps have been installed on the effluent line from each column. An automatic sampling device collects separate 200-ml samples of column effluent for analysis every four hours, and, in addition, 24-hour composite samples of effluent are drawn into the 200-liter reservoirs shown in Figure 10.

All studies to date have been carried out at a flow rate of 5 gpm/ft^2 (204 l/min/sq m), and effectiveness of treatment has been measured in terms of chemical oxygen demand and total organic carbon.

RESULTS

The in-plant comparison of fluid-column and packed-column methods for operation of adsorption has vividly demonstrated at least one point; namely, packed-column operation for direct treatment of secondary sewage effluents, even with the relatively large 0.503-mm carbon employed in the present studies, is beset with considerable problems of clogging and maintenance of flow. Even with pumping into and out of the packed-column, as indicated in Figure 10, it has been impossible to maintain any significant flow after 10-12 hours of operation. Conversely, the fluid-column has given no problems of flow control and no indication of significant increase in losses after 16 days of continuous operation. The operational advantage of the latter method for contacting carbon with a waste water is obvious.

Figure 11 is a plot of cumulative adsorption of COD by the 2000-gram charge of carbon in the fluid column. Because influent concentration of COD varied with time in this experiment, this quantity is also plotted cumulatively. It is apparent from the data plotted in Figure 11 that the adsorption column does react to variations in influent concentration, as evidenced by the coincidence of sharp increases in cumulative amount adsorbed with sharp increases in cumulative input.

From the beginning of the run up to the 16th day of operation the fluid-carbon column continually averaged about 50% reduction in COD. That is, the column was approximately as efficient for COD removal on the 16th day as it was on the 1st day. This fact gives indication that the carbon had not yet achieved a significant extent of saturation after 16 days, but that at the given flow rate the length (approximately 3 meters expanded) of the column of carbon was not sufficient to permit reductions in COD much in excess of 50%. In other words, it appears that the effective contact time of the waste with the carbon was not sufficient to achieve greater percent reductions. For this reason alone the run was terminated after the 16th day of operation. It is quite significant that up to the time of termination the column had adsorbed 465 grams of COD, for a COD-%-weight capacity of over 23%.

In-plant studies are presently being carried out on the effects of increasing contact of the waste with carbon by employing fluid-columns in series. Also, various methods of pretreatment of the waste are being tested with the objective of decreasing unnecessary loading of the carbon columns.

SUMMARY

The advantages of the fluid-column method for contacting carbon with waste waters over the packed-column method have been clearly demonstrated in the present studies. A biologically-treated sewage effluent has been shown to completely clog a 1.83-meter depth of 0.503-mm carbon within a few hours during packed-column operation, whereas a parallel fluid-column operation under the same conditions has shown no tendency for clogging or excessive head losses after 16 days. Laboratory studies - not cited in the text - on comparison of packed-column and fluid-column operations have indicated further that even with solutions containing no particulate matter packed columns rapidly develop much higher head losses than fluid columns, to the point of rendering the former mode of operation impractical. Two laboratory columns, one containing 0.359-mm carbon and the other 0.273-mm carbon, each approximately 22 cm in depth, were contacted with a 75-μmol/l solution of sulfonated alkylbenzene in distilled water. Even with the short columns and an available head of 3 meters, it was not possible in these studies to maintain the initial flow rate of 2.5 gpm/sq.ft (102 l/min/sq.m). Within 24 hours the flow rate in each experiment had dropped to less than one-half of the initial rate, and to less than one-tenth within 30 hours. There appeared to be adhesion of carbon particles to each other within the columns, quite probably as a result of a surface build-up of adsorbate.

Relative to adsorption patterns in fluid columns, definite differences have been noted for different types of solutes. For two substances within a given chemical class, it has been observed that the member of higher molecular weight is removed more completely from solution during the very early stages of operation but increases more rapidly in leakage through the column as operation continues into intermediate stages of breakthrough. However, a sharper complete breakthrough then occurs for the material of lower molecular weight while adsorption continues for the high-weight substance. This behavior has been found to be predictable, qualitatively, from non-flow system measurements of adsorption parameters for the materials in question. A logical explanation for the observed patterns is that the high molecular weight material has a greater energy for adsorption(2) and is thus removed more completely during the inital stages. However, the transport of the larger molecules into the pore structure of the carbon proceeds slowly(1), so that active external sites soon reach a significant fraction of saturation and subsequent adsorption is less rapidly effective for the material of high molecular weight. A delayed, but sharper, breakthrough obtains for the small-molecule substance which is able to more rapidly penetrate the pore structure(1) so that external sites maintain a high degree of activity for a longer period of time. Thus, only when nearly full capacity has been attained for the low-weight compound will a significant and sharp breakthrough occur. Because the ultimate capacity for adsorption of the high-weight material is greater however(2), adsorption will continue beyond the point in operation at which complete breakthrough of the low-weight substance occurs.

Normal temperature and pH variations have been observed to have little effect on adsorption in fluid-carbon columns. However, observed effects of pH suggest some possibility for enhancing adsorption in certain special situations by acidification of the influent to the adsorption column.

Definite competition for adsorption between the components of heterogeneous solutions has been noted. Two observations relative to this competition are: the effects become more pronounced as the carbon more nearly approaches saturation; and the total capacity for adsorption in fluid-carbon columns is greater for a mixed solution of given total concentration than for a single-solute solution of any of the components in like concentration. These observations suggest the existence of a range of adsorption sites of varying specificity and activity for active carbon.

Finally, it has been demonstrated that very high capacities, with resulting economy, can be realized for active carbon under proper conditions of operation in fluid-columns. Capacities up to 40% by-weight have been attained for heterogeneous solutions. Capacities of this order represent a significant increase over the 15-20% capacities normally realized with more coarse particles in packed-column operation.

ACKNOWLEDGEMENTS

Messrs. J.P. Gould, T.M. Keinath, and J.G. Kim are thanked for their assistance during the experimental phases of the present work. These studies have been supported in part by the Advanced Waste Treatment Research Program of the U.S. Public Health Service and in part by Research Grant WP00706 from the U.S. Public Health Service, Division of Water Supply and Pollution Control.

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FIGURE CAPTIONS

Figure 1. - COMPARATIVE BREAKTHROUGH PATTERNS FOR A BRANCHED-CHAIN SULFONATED ALKYLBENZENE (ABS) AND p-- TOLUENE-SULFONATE

Figure 2. - BREAKTHROUGH PATTERNS FOR SOLUTIONS OF DIFFERENT INITIAL CONCENTRATION

Figure 3. - CUMULATIVE ADSORPTION FROM SOLUTIONS OF DIFFERENT INITIAL CONCENTRATION

Figure 4. - EFFECT OF ACIDIFICATION ON BREAKTHROUGH PATTERN

Figure 5. - CUMULATIVE ADSORPTION FROM SOLUTIONS OF DIFFERENT pH

Figure 6. - BREAKTHROUGH PATTERNS FOR SULFONATED ALKYLBENZENE (ABS), 2-sec-BUTYL-4,6-DINITROPHENOL (DNOSBP), AND QUININE IN A THREE-SOLUTE SOLUTION

Figure 7. - COMPARATIVE BREAKTHROUGH PATTERNS FOR SULFONATED ALKYLBENZENE (ABS) IN A SINGLE-SOLUTE SOLUTION AND IN A THREE-SOLUTE SOLUTION WITH 2-sec-BUTYL-4,6-DINITROPHENOL (DNOSBP), AND QUININE

Figure 8. - CUMULATIVE ADSORPTION OF THE COMPONENTS OF A MIXTURE OF SULFONATED ALKYLBENZENE (ABS), 2-sec-BUTYL-4,6-DINITROPHENOL (DNOSBP), AND QUININE

Figure 9. - CUMULATIVE ADSORPTION OF ORGANIC CARBON FROM A MIXTURE OF SULFONATED ALKYLBENZENE (ABS), 2,4-DICHLOROPHENOL (2,4-DCP), NONYLPHENOXYPOLYETHOXYETHANOL (9N10), AND TRIETHANOLAMINE (TEA)

Figure 10. - SCHEMATIC REPRESENTATION OF EXPERIMENTAL APPARATUS FOR IN-PLANT INVESTIGATIONS

Figure 11. - CUMULATIVE COD-LOADING AND COD-ADSORPTION FOR FLUID-CARBON COLUMN

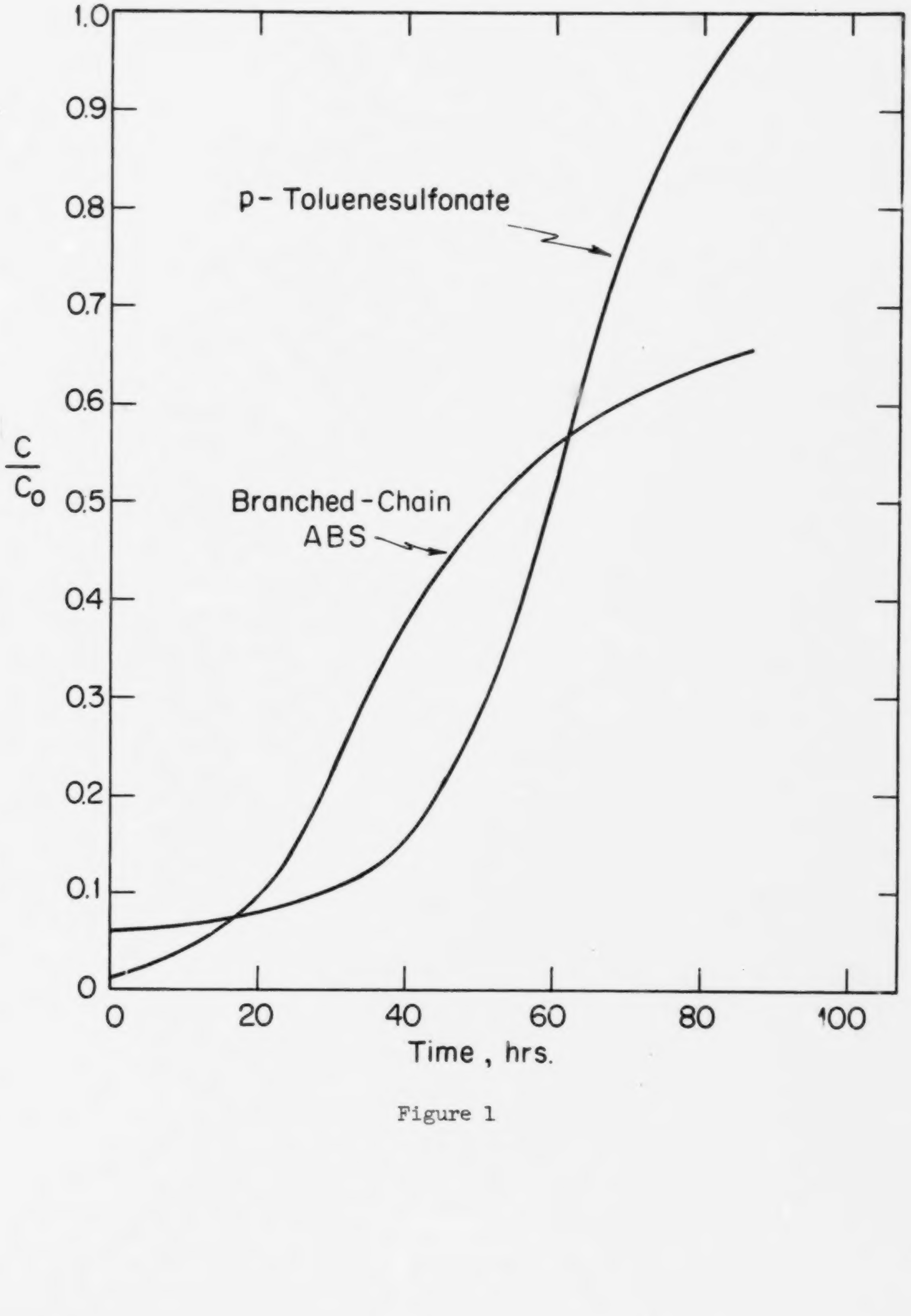
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
C/C_o
p- Toluenesulfonate
Branched - Chain ABS
0
20
40
60
80
100
Time , hrs.

Figure 1

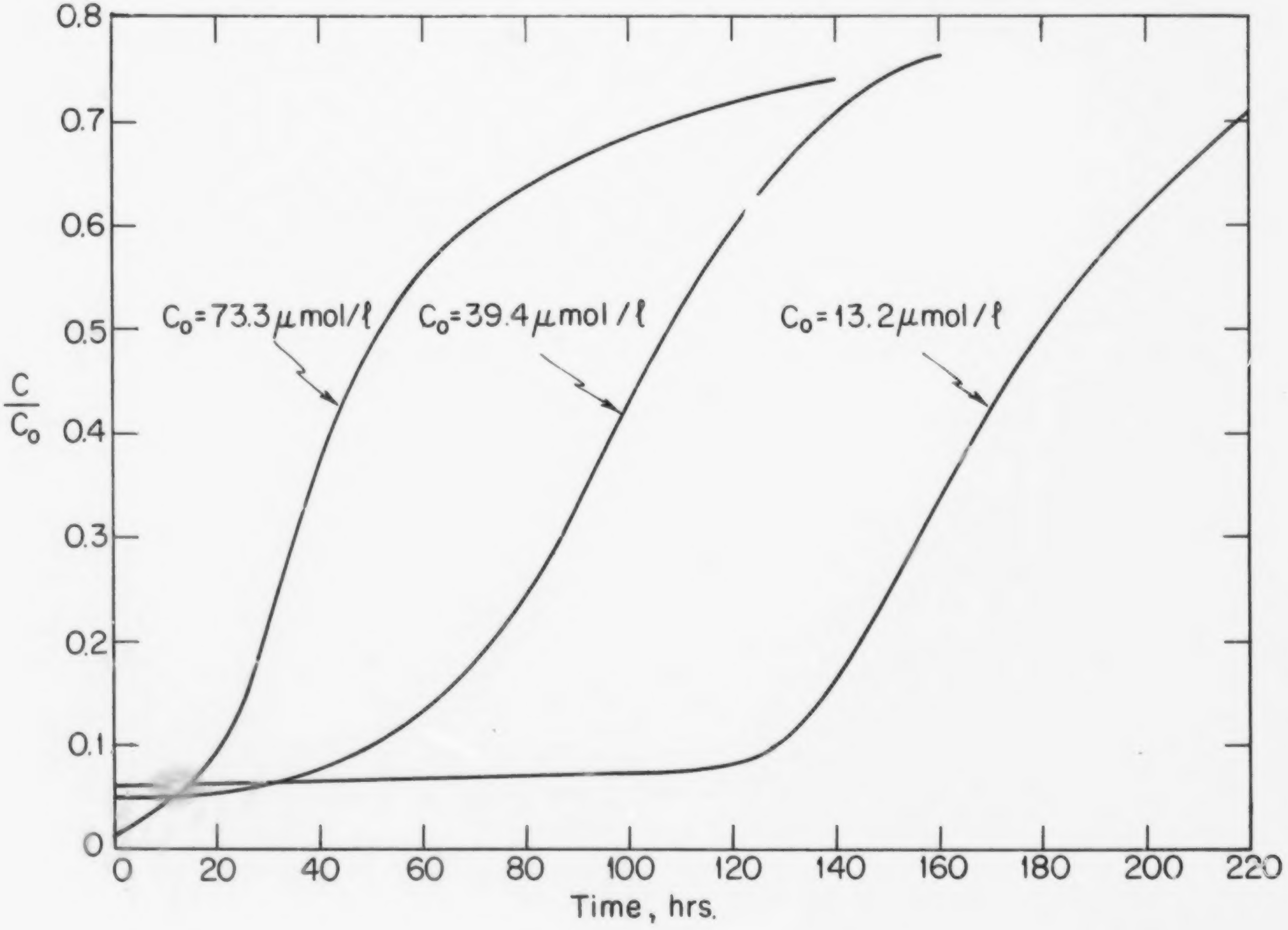
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
$\frac{C}{C_o}$
$C_o = 73.3\,\mu mol/\ell$
$C_o = 39.4\,\mu mol/\ell$
$C_o = 13.2\,\mu mol/\ell$
0
20
40
60
80
100
120
140
160
180
200
220
Time, hrs.

Figure 2

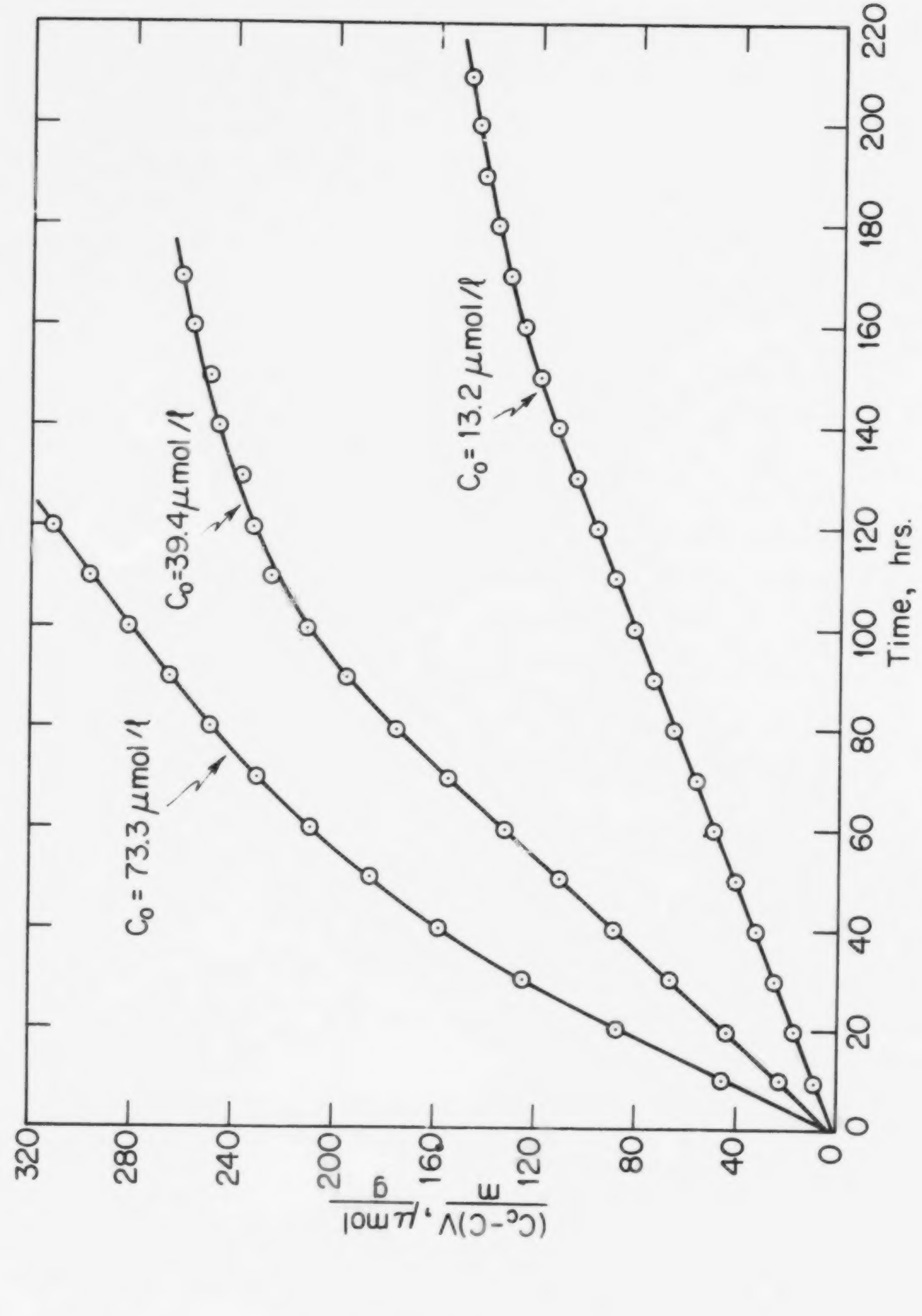
$\frac{(C_o - C)V}{m}$, μmol/g
0
40
80
120
160
200
240
280
320
Time, hrs.
0
20
40
60
80
100
120
140
160
180
200
220
C_o = 73.3 μmol/l
C_o=39.4 μmol/l
C_o = 13.2 μmol/l

Figure 3

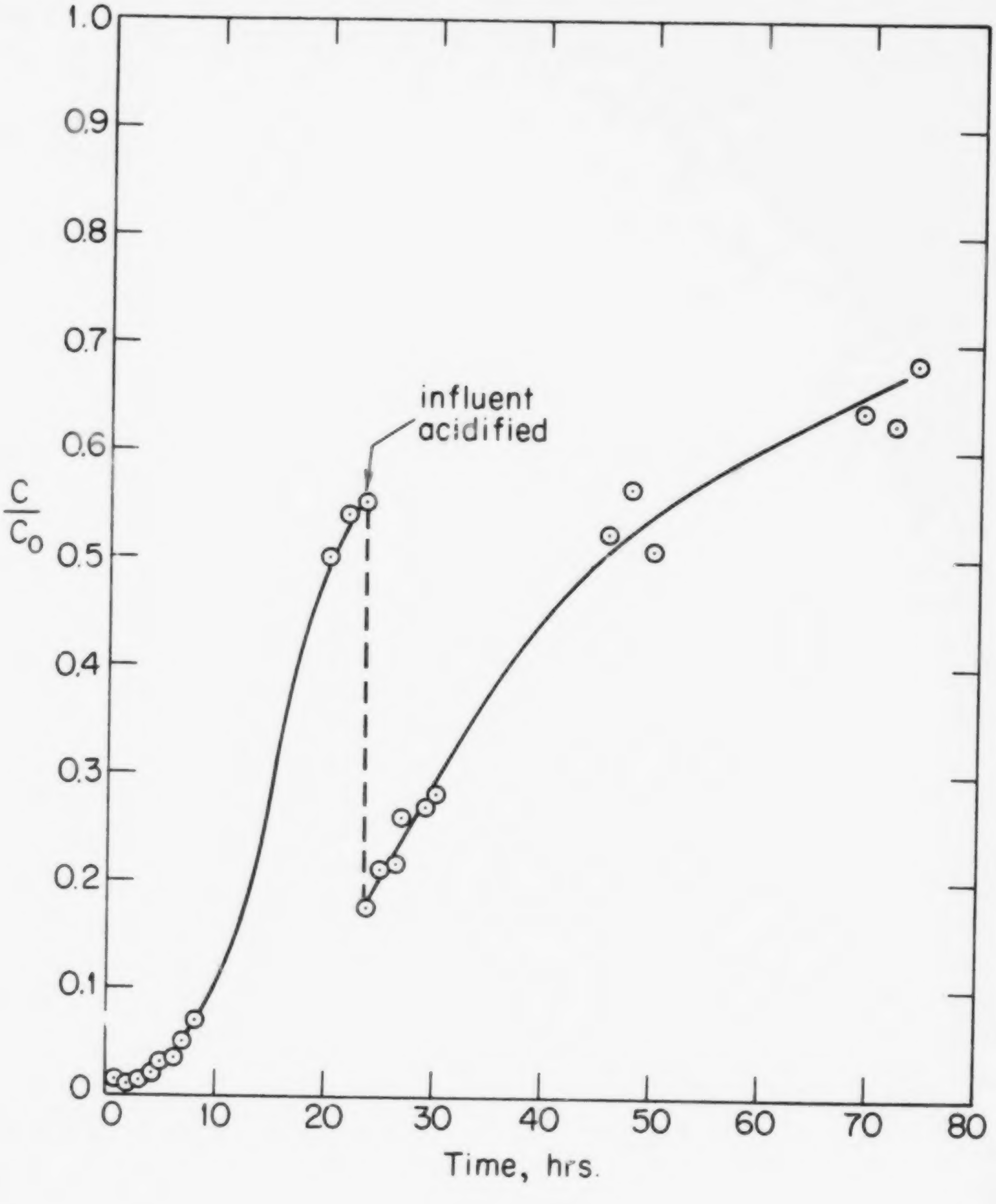
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
$\frac{C}{C_0}$
influent acidified
0
10
20
30
40
50
60
70
80
Time, hrs.

Figure 4

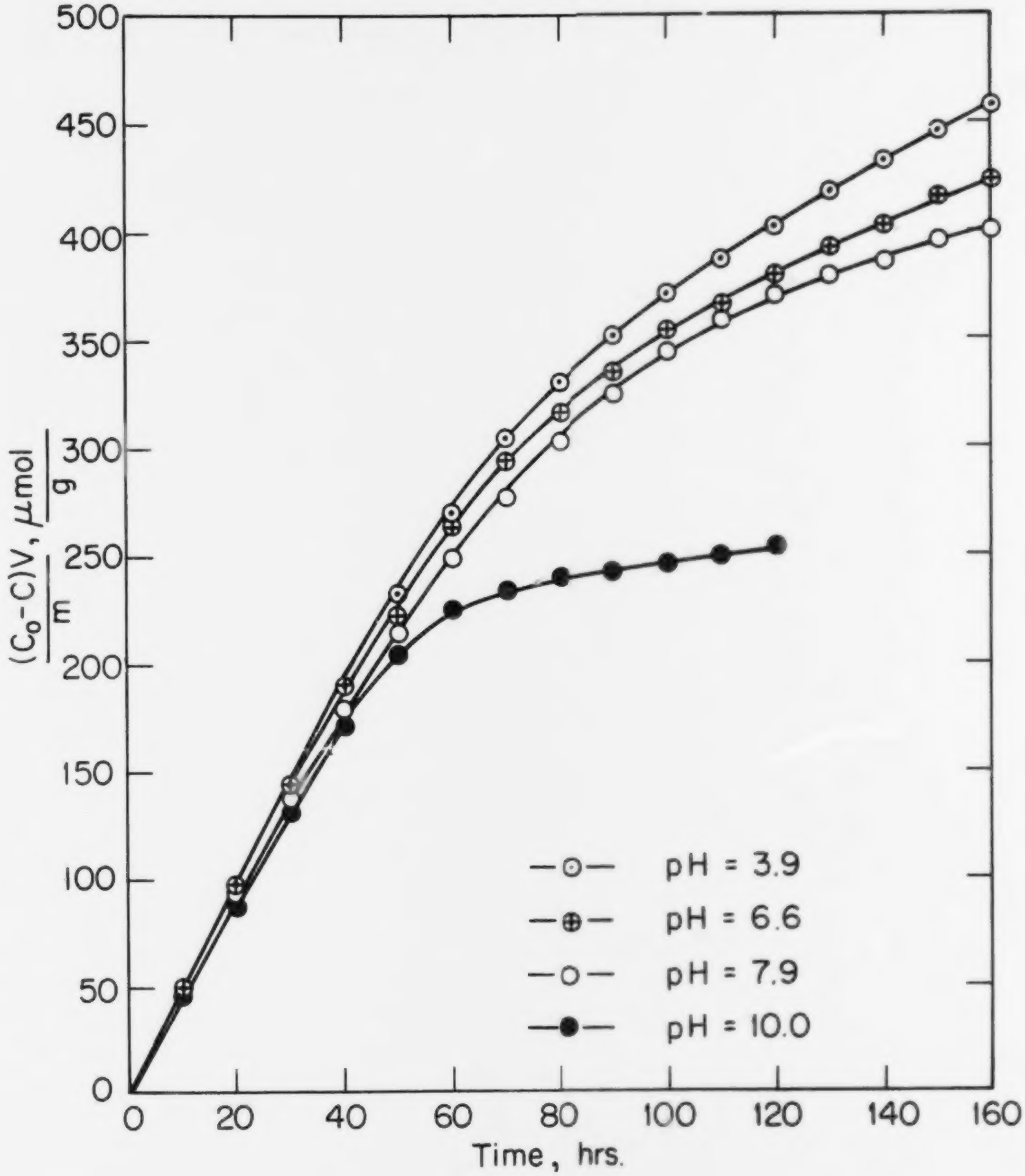
500
450
400
350
300
250
200
150
100
50
0
$\frac{(C_o - C)V}{m}, \frac{\mu mol}{g}$
0
20
40
60
80
100
120
140
160
Time, hrs.
⊙ pH = 3.9
⊕ pH = 6.6
○ pH = 7.9
● pH = 10.0

Figure 5

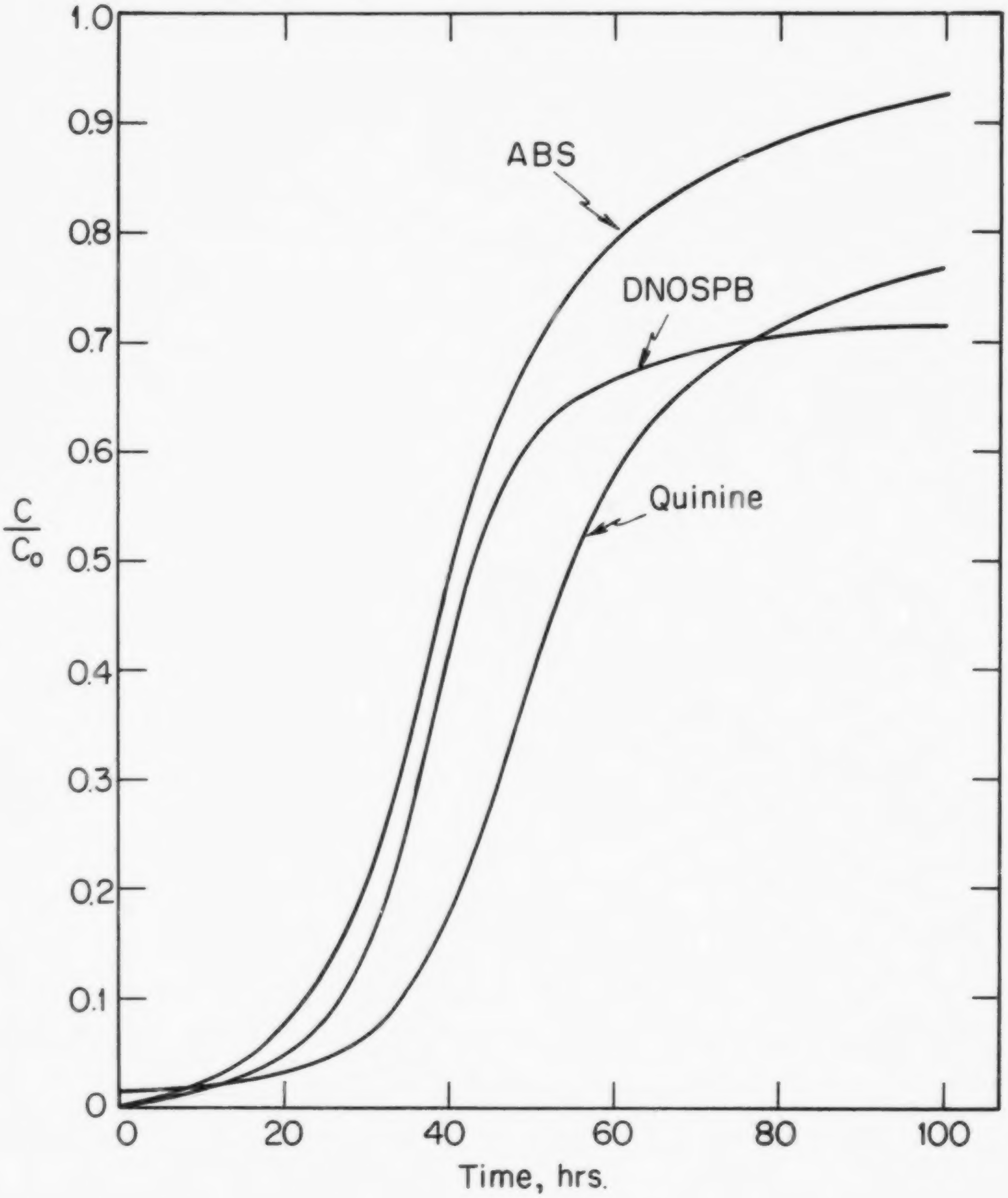
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
C/C₀
0
20
40
60
80
100
Time, hrs.
ABS
DNOSPB
Quinine

Figure 6

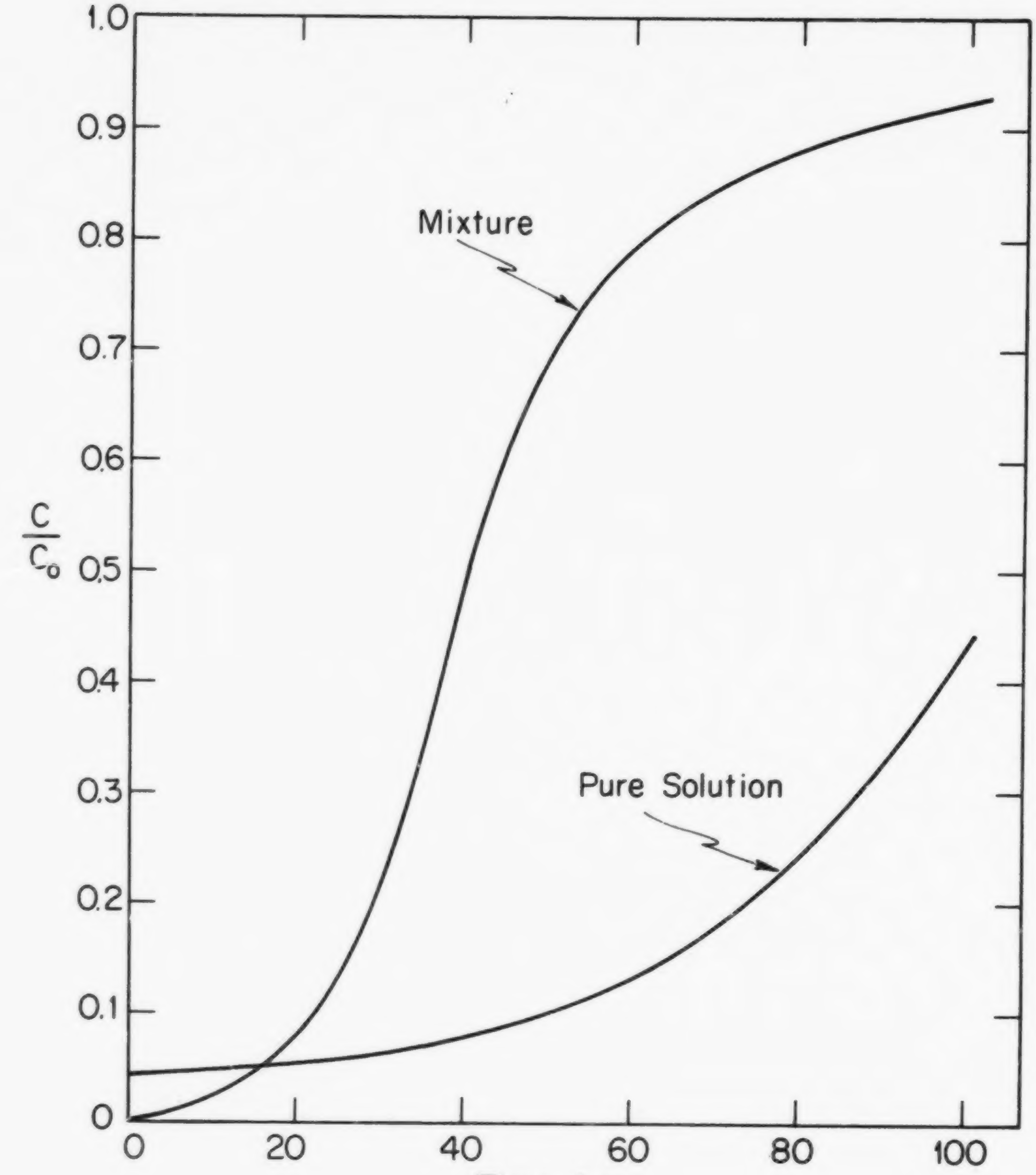
1.0
0.9
0.8
0.7
0.6
$\frac{C}{C_o}$
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
100
Time, hrs.
Mixture
Pure Solution

Figure 7

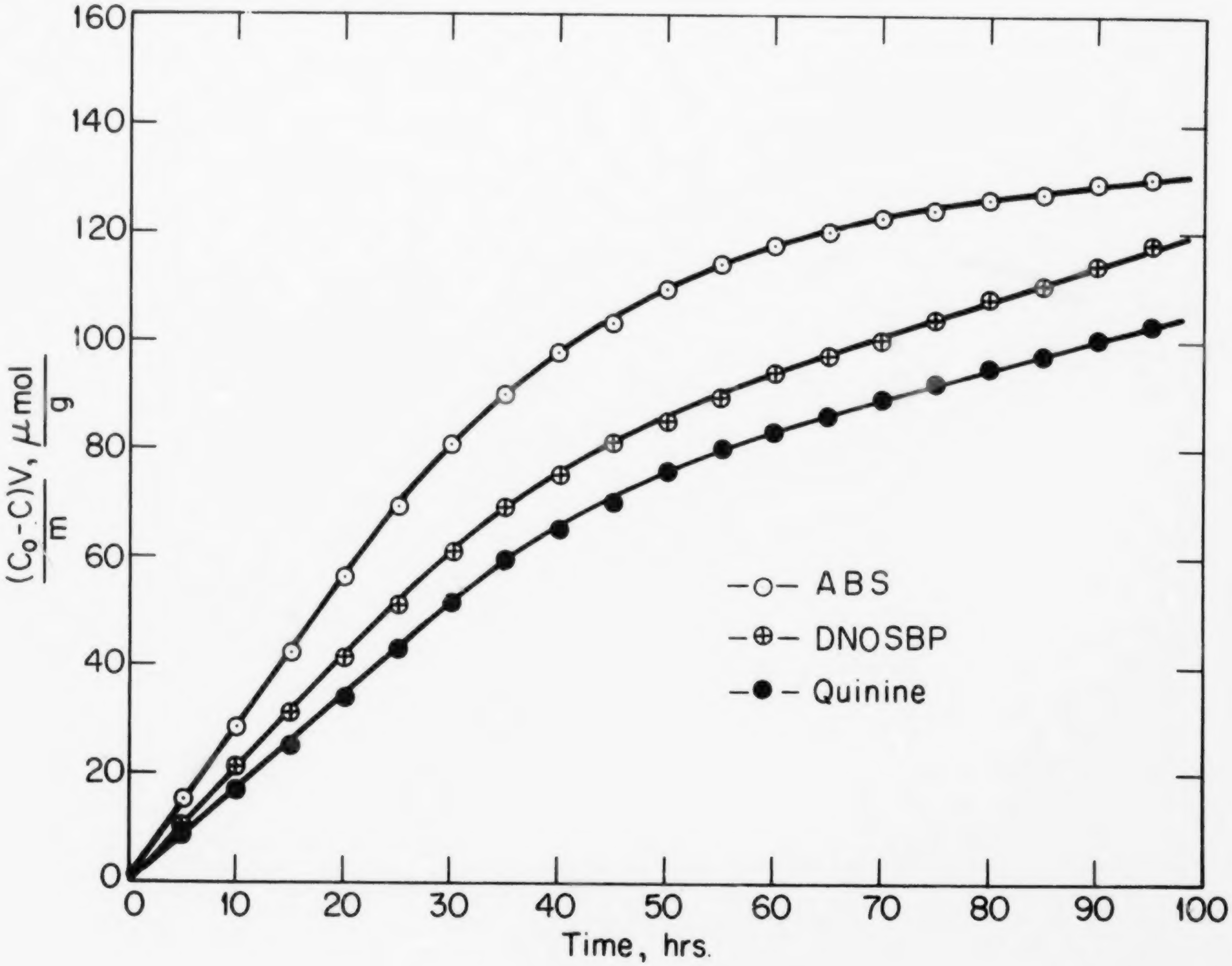
160
140
120
100
80
60
40
20
0
$\frac{(C_o-C)V}{m}, \frac{\mu mol}{g}$
0
10
20
30
40
50
60
70
80
90
100
Time, hrs.
ABS
DNOSBP
Quinine

Figure 8

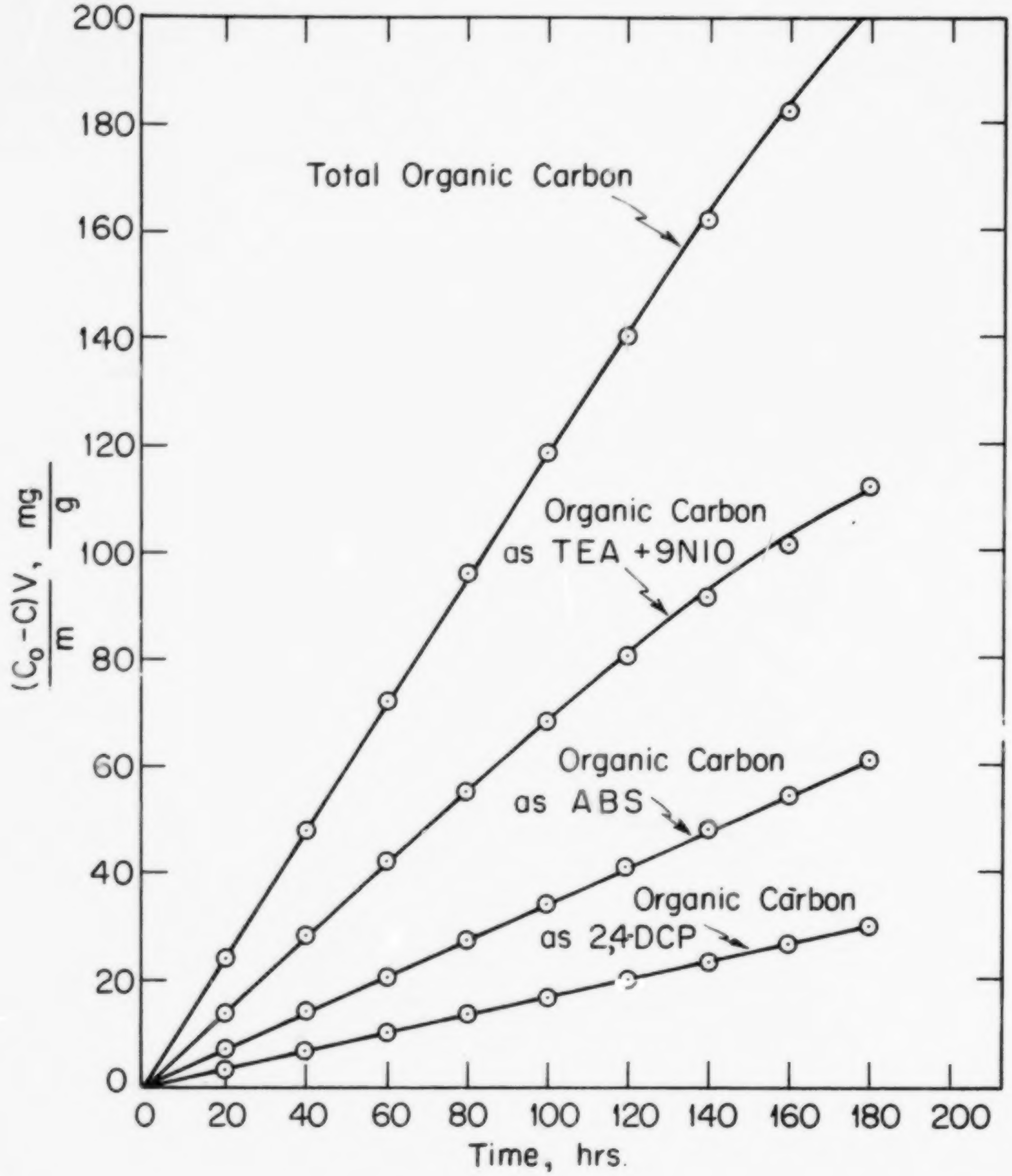
$\frac{(C_o - C)V}{m}, \frac{mg}{g}$
0
20
40
60
80
100
120
140
160
180
200
Time, hrs.
0
20
40
60
80
100
120
140
160
180
200
Total Organic Carbon
Organic Carbon as TEA +9N10
Organic Carbon as ABS
Organic Carbon as 2,4-DCP

Figure 9

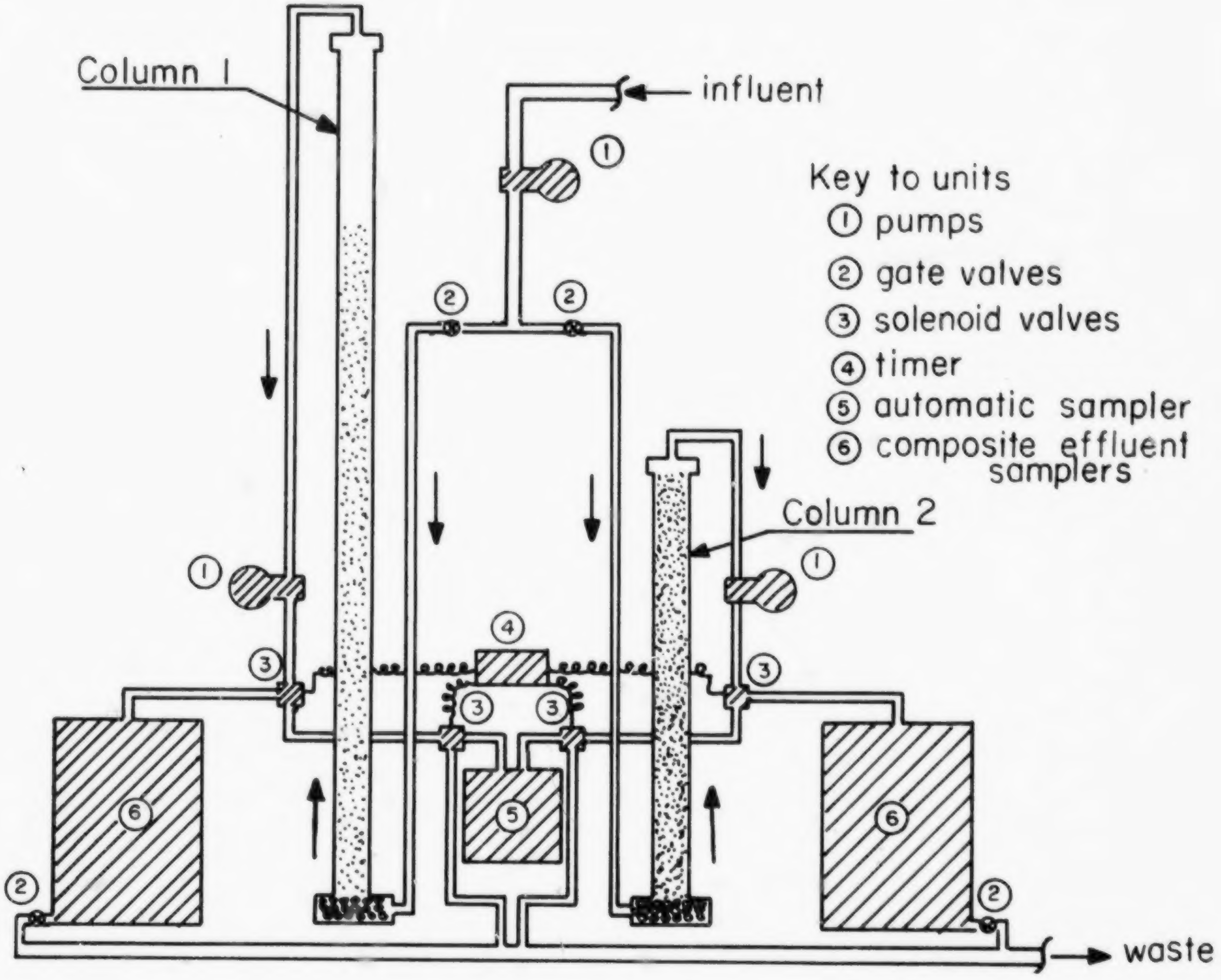
Column 1
influent
Key to units
① pumps
② gate valves
③ solenoid valves
④ timer
⑤ automatic sampler
⑥ composite effluent samplers
Column 2
①
②
③
④
⑤
⑥
waste

Figure 10

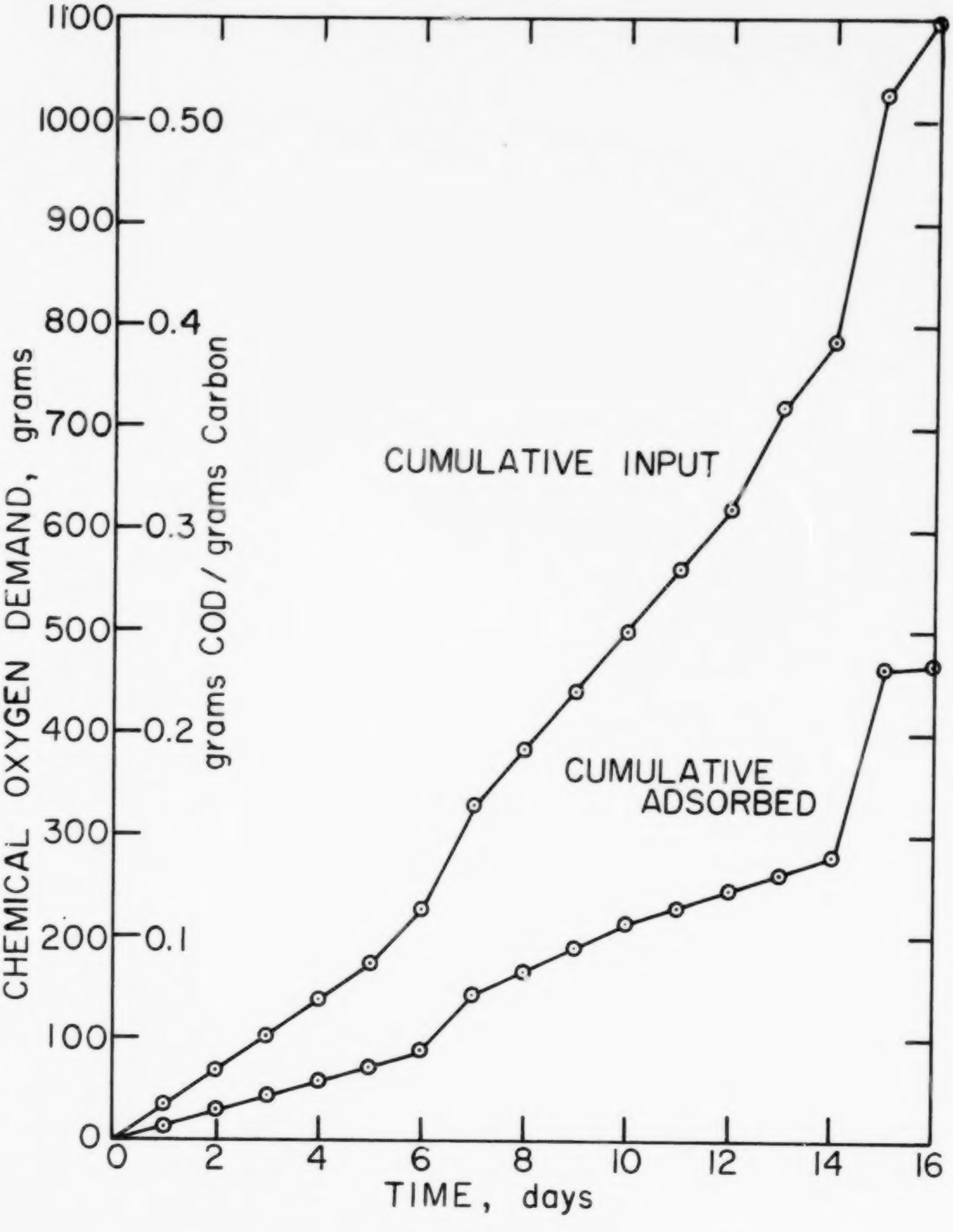
CHEMICAL OXYGEN DEMAND, grams
grams COD / grams Carbon
0
100
200
300
400
500
600
700
800
900
1000
1100
0.1
0.2
0.3
0.4
0.50
TIME, days
0
2
4
6
8
10
12
14
16
CUMULATIVE INPUT
CUMULATIVE ADSORBED

Figure 11

Prepublication Manuscript

Not for Citation or General Distribution

MASS TRANSFER RATES FOR WATER AND WASTE POLLUTANTS IN FLUIDIZED ADSORBERS*

Walter J. Weber, Jr. and Thomas M. Keinath**

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* Paper presented at National Meeting of the American Institute of Chemical Engineers Symposium on Research on Adsorption, Detroit, Michigan, Dec. 8, 1966 (to be published in Symposium Proceedings).

** Assoc. Prof. and Research Fellow, respectively, Dept. of Civil Engineering, The Univ. of Michigan, Ann Arbor, Michigan.

Adsorption on active carbon has for some time been recognized in the chemical industries as an effective unit operation for a wide range of solute-solvent separations. Interest has recently focused on the possibility of applying this operation for treatment of domestic and industrial wastewaters for removal of synthetic organic substances which resist removal by more classical waste treatment methods. This interest has double impetus. First, the range and complexity of resistant or persistent pollutants is increasing in direct proportion to the expanding technology of the chemical industries. Concomitantly, increasing public demand for more stringent control of water pollution must be recognized and met.

Direct extrapolation of operating conditions for adsorption from relatively straight-forward process applications to wastewater treatment applications is not feasible. Definition of conditions for most effective and efficient use of adsorption on active carbon in the latter application is complicated by the heterogeneity of the solute system, by the variability in concentration and composition of the waste components, by the presence of particulate matter and dissolved gases, and by the variability and relative lack of control of systemic variables such as pH. These and similar characteristics of wastewaters must dictate the method and specific conditions of operation. However, certain qualitative operating criteria can be set forth on the basis of knowledge of the general behavior of adsorption systems. By way of example, the desirability of utilizing as small an adsorbent particle size as operational conditions permit is well recognized. Also, because of the nature of adsorption equilibria, flow-through operation has some advantages over batch-type operation. Conversely, with particulate matter in the solution being treated, fine adsorbent particle sizes can lead to serious problems of clogging and severe head loss in columnar operation with packed beds. Further, the presence of dissolved gases can produce problems of air binding with packed-column type operation.

One method for taking advantage of fine adsorbent particle size and yet avoiding head-loss and air binding problems normally associated with packed-bed operation with fine media is to employ a fluidized-solids contacting technique. It is the nature of this type of operation with systems comprised of dissolved materials representative of persistent organic pollutants that is the subject of the present work. Some previous work on the adsorption of the same and similar persistent pollutants on active carbon has been directed toward evaluation of the characteristics of this process in rapidly agitated non-flow systems.(1,2) Subsequent preliminary investigation of rates of adsorption from aqueous solution in fluidized-solids contactors has provided the groundwork for the present studies.(3)

EXPERIMENTAL

Experimental Columns

The experimental up-flow columns consisted of Lucite tubes, 1 inch in diameter and 3 feet in length. Each column was equipped at its base with a distribution chamber filled with 2-mm glass beads which served to dissipate the velocity head at the influent section, thus ensuring steady-state, one-dimensional flow along the length of the column. A 140-mesh stainless steel screen supported the carbon in the column and separated it from the glass beads in the distribution chamber. Flow to the column from a constant head tank was regulated by means of needle-valve controls. Effluent from the column was passed through an air-gap to prevent siphoning, through a 1-liter sedimentation basin which functioned to remove any fine particulate matter carried over in the effluent, and finally into one of several volume-calibrated collection reservoirs. Samples of total effluent were collected and analyzed at appropriate intervals to provide total solute uptake data for the fluidized carbon columns.

Active Carbon

A coconut-base active carbon was utilized for the majority of the laboratory studies; this was Columbia LC grade obtained from the National Carbon Company. In addition, one column study was carried out with a coal-base carbon, grade SGL, from the Pittsburgh Activated Carbon Company.

The carbons were prepared for use in the column studies first by fractionation into uniform particle sizes through sieving. Fractions of selected size ranges were then carefully washed with distilled water and dried at 105°C. A set of United States Standard Sieves was utilized for fractionation.

Solutes

A number of organic solutes typical of different classes of organic pollutants were chosen for study largely on the basis of recognized occurrence and persistence in wastewaters. Some of the studies, designated as Columns A through I in Table 1, were conducted either with a branched chain sulfonated alkylbenzene obtained as a 92.9% active-material sodium salt from the Petrochemical Department of the Continental Oil Company or with a similar material, Utrawet DS, obtained from the Atlantic Refining Company. Each of these two solutes was determined by spectrophotometric methods to have an average molecular weight of 372.(4) Ultrawet K, another branched-chain sulfonated alkylbenzene obtained from the Atlantic Refining Company, was utilized for the studies designated as Columns J through T in Table 1. Other solutes, studied largely for their competitive adsorption effects in mixed solutions with the sulfonated alkylbenzenes, included nonylphenoxypolyethoxyethanol (9N10) and 2-sec-butyl-4,6-dinitrophenol (DNOSBP) (from the Dow Chemical Company) as well as triethanolamine (TEA), 2,4-dichlorophenol (2,4-DCP), and quinine sulfate (all reagent grade products from Eastman Organic Chemicals).

Analytical Methods

Ultraviolet spectrophotometry was used for determination of concentrations of the sulfonated alkylbenzenes in studies (A through T) in which this solute was the only adsorbate present in solution. Absorbance measurements for this material were carried out at 225 mμ, at which wavelength the molar absorptivity has a value of 12 9 x 10^6 cm^2/mol.(4) For those studies in which a sulfonated alkylbenzene was but one component of a multicomponent solution in which the other solutes caused interference with the ultraviolet method, the Longwell and Maniece modification of the Jones method using methylene blue was employed.(5)

Several of the other compounds studied are subject to analysis by visible and ultraviolet spectrophotometric methods. Quinine exhibits a maximum light absorbance at 330 mμ with a molar absorptivity of 4.20×10^6 cm^2/mol; 2,4-dichlorophenol has a maximum absorbance at 284 mμ with a molar absorptivity of 2.05×10^6 cm^2/mol; and 2-sec-butyl-4,6-dinitrophenol has a maximum absorbance at 375 mμ with a molar absorptivity of 13.80×10^6 cm^2/mol. Each of these components was found to follow the Beer-Lambert law for the range of concentrations studied.

The remaining solutes, triethanolamine and nonylphenoxypolyethoxyethanol, were studied only as components in a complex mixture of organic compounds, and determination of their individual concentration not made. Rather, effectiveness of adsorption in the complex mixture of which triethanolamine and nonylphenoxypolyethoxyethanol were components was evaluated in terms of the overall removel of organic matter, measured in terms of total organic carbon. Determinations of organic carbon were made according to a high-temperature wet oxidation method.(6)

RATE RELATIONSHIPS

Previous work has demonstrated that rate of uptake of solutes similar to those used in the present studies by porous carbon in rapidly agitated non-flow systems is controlled by intraparticle transport.(7,8) However, for columnar flow-through operation in which flow velocities are in the neighborhood of .34 mm/sec to 2.04 mm/sec., one would expect that initial rate of uptake of solute would likely be controlled by film transport at the external surface of the adsorbent. Intraparticle transport in such low velocity flow-through systems should enter as a rate controlling mechanism only in later stages of column operation.

Based on the assumption of film transport, a relatively simple rate relationship can be set forth for the initial stages of adsorption in the experimental fluidized carbon columns. If the quantity $(C_o-C)V/m$ is used to represent the uptake of solute per unit mass of adsorbent at any point in time, then the rate of transfer of solute from bulk solution to the adsorbent can be described by the expression

$$\frac{\left(d\,\frac{(C_o-C)V}{m}\right)}{dt} = k\ S\ (C_s-\bar{C}) \text{ --------------- } (1)$$

in which k is the external mass transfer coefficient, C_s the concentration of adsorbing solute at the liquid surface side of the interfacial film, C the concentration of solute in the effluent from the column, $\bar{C}$ the concentration of solute at the solid surface side of the interfacial film, C_o the concentration of solute in the influent to the column, V the throughput volume of solution, m the total mass of the adsorbent in the column, and S the external surface area per unit mass of adsorbent.

For fluidized operation, in which adsorbent particles are for all practical purposes completely mixed over the length of the column, the value of $\bar{C}$ should be uniform throughout the bed. The quantity C_s will of course vary logarithmically over the length of the column. However, during initial stages of operation, breakthrough of solute is negligible. For this condition the log-mean value for C_s remains essentially constant and is a constant multiple of C_o, consequently one may substitute C_o for C_s in Equation 1 and include the constant multiplier in the mass transfer coefficient, k.

For all practical purposes the concentration, $\bar{C}$, of solute at the solid surface side of the interfacial film can be neglected during the initial stages of adsorption, in which case Equation 1 reduces to

$$\frac{\left(d\,\frac{(C_o-C)\,V}{m}\right)}{dt} = k\;S\;C_o \text{ ------------------- } (2)$$

The rate of uptake then is proportional to the transfer coefficient, the external surface area, and the concentration of solute in the influent to the column. Equation 2 is thus a useful expression for characterization and definition of transfer rates for solute uptake in fluidized columns. Pursuant to a characterization of the effect of systemic variables on transfer rates, the present studies have included exploration of: a) effect of flow rate on transfer rate; b) dependence of transfer rate on particle size of the adsorbent; c) effects of solute concentration; d) pH effects; e) temperature dependence; and f) competitive effects in three-component and four-component multisolute systems.

RESULTS

Twenty fluid-bed studies were conducted with single-solute solutions of sulfonated alkylbenzene. Columbia LC carbon was used for all of these studies. Table 1 contains a listing of the salient properties of each of the 20 single-solute systems. In addition, two experiments were carried out with multicomponent solutions to determine the extent of competitive interactions in heterogeneous systems and to evaluate the influence of these interactions on mass transfer rates for the individual components of the mixture. Pittsburgh SGL carbon was used in one of the multisolute studies and Columbia LC carbon in the other.

TABLE 1

SYSTEMIC PROPERTIES OF EXPERIMENTAL FLUIDIZED CARBON COLUMNS FOR SINGLE-SOLUTE STUDIES

Column	Particle Size, (mm)	C_o (μmol/liter)	Flow Rate, (gpm/ft^2)	Surface Area, S, (cm^2/gm)	Mass Transfer Rate, ($\frac{\mu\text{-mols}}{\text{g-hr}}$)	k x 10^4 (cm/hr)	$N_{Re'}$
A	.273	67.0	2.75	451	4.54	1.50	0.55
B	.273	65.0	1.43	451	2.37	0.81	0.29
C	.273	68.4	6.14	451	10.25	3.32	1.22
D	.273	69.4	0.68	451	1.20	0.384	0.14
E	.178	76.1	2.56	665	4.90	0.969	0.33
F	.503	78.5	2.52	245	4.90	2.55	0.92
G	.359	78.5	2.58	342	4.90	1.83	0.68
H	.230	74.9	2.52	534	4.90	1.23	0.42
I	.273	73.7	2.58	451	4.90	1.46	0.52
J	.273	73.3	2.50	451	4.28	1.29	0.52
K	.273	39.4	2.50	451	2.20	1.24	0.52
L	.273	13.2	2.50	451	0.81	1.36	0.52
M	.273	77.1	2.20	451	3.20	0.92	0.52
N*	.273	78.9	2.50	451	4.90	1.38	0.52
O*	.273	78.9	2.50	451	4.90	1.38	0.52
P*	.273	78.9	2.50	451	4.55	1.28	0.52
Q*	.273	78.9	2.50	451	4.33	1.22	0.52
R**	.273	78.5	2.50	451	4.30	1.23	0.52
S**	.273	78.5	2.50	451	4.30	1.23	0.52
T**	.273	78.5	2.50	451	4.30	1.23	0.52

Note: All studies were carried out with 45 grams of Columbia LC carbon except Column M in which 52.1 grams was used.

* pH studied as a variable, ** temperature studied as a variable

Flow Rate as a Variable

Columns A through D represent experiments in which the effects of different flow rates on the mass transfer coefficient as defined in Equation 2 were studied. Figure 1 shows cumulative uptake of sulfonated alkylbenzene by carbon as a function of time for different flow rates. Each of the four experimental columns contained 45 grams of 0.273-mm Columbia carbon, while influent concentrations of solute were maintained at levels in the range of 67-70 μmoles/liter.

The effect of flow rate on the solute uptake curves shown in Figure 1 accords well with expected behavior. Equation 2 is based on the assumption that film diffusion is rate-limiting in the early portions of a column run. Increased flow rate in this region may be expected to result in a compression or reduction of the surface film, thereby decreasing resistance to mass transfer and increasing the mass transfer rate. Figure 2 illustrates rather well the fact that film diffusion is rate limiting at the outset of a column study, as good correlation obtains between flow rate and the mass transfer rate.

Equation 2 indicates that for the postulated rate step the initial portion of a plot of adsorbate uptake per unit weight of adsorbent vs. time should approach linearity, with a slope of $k\ S\ C_o$. As Figure 1 illustrates, this linear portion exists for each of the flow rate studies. The lower the flow rate the more marked is the influence of film diffusion and the longer the linear portion of the curve. Deviations from linearity occur because of the increasing influence of intraparticle transport on the overall rate of mass transfer as each run progresses.

Particle Size as a Variable

Five experiments (Columns E - I) were carried out with sulfonated alkylbenzene as the solute and Columbia LC carbon of different particle sizes - 0.178 mm, 0.230 mm, 0.273 mm, 0.359 mm, and 0.503 mm - as the adsorbent. Flow rates of approximately 2.5 gpm/ft^2 were maintained in columns containing 45 grams of the carbon. The initial concentration of solute in each experiment was nearly identical, in the range of 75 to 79 μmols per liter.

The uptake versus time curves for the several particle sizes are shown in Figure 3. In this plot it may be observed that the initial mass transfer rates are very nearly equivalent. A tabulation of the mass transfer rates for Columns E - I in Table 1 reveals that these rates are indeed all equal to 4.90 μmols/g-hr. Equation 2 illustrates that the mass transfer coefficient should be inversely proportional to the external surface area. This is verified in the present experiments, as illustrated in Figure 4, in which data from Columns E - I demonstrate a linear dependence of the transfer coefficient on the reciprocal of the external surface area.

In Figure 3 one can observe that for smaller particle sizes the initial linear portion of the uptake curves extend over longer periods of time, indicating that film diffusion remains rate-limiting for longer periods. This observation may be explained by considering that film diffusion continues as the rate-determining step until such time as the external surface area becomes essentially saturated with solute, at which point intraparticle transport becomes rate determining. Since the surface area per unit weight of carbon increases for decreasing particle sizes, the film diffusion step remains rate limiting for longer periods of time for smaller particle sizes, as more time is required to saturate the greater external surface areas.

Particle size and flow rate are both characterized in the dimensionless Reynolds number, N_{Re}. This group is thus useful for correlation of transfer coefficients determined from the present experiments with fluid-carbon columns under different conditions of flow rate and particle size. For calculation of values for a modified Reynolds number, $N_{Re'} = \frac{VD\rho}{\mu}$; the velocity term v has been taken as the superficial face velocity of flow through the column. The terms D, ρ, and μ in the Reynolds group are, respectively, the particle diameter, and the density and viscosity of water. In Figure 5 values of ln k are plotted against values of ln $N_{Re'}$. The data shows good correlation, indicating that the transfer coefficient is an adequate tool, over the range taken, for description of rates of adsorption in the experimental fluidized columns.

Solute Concentration as a Variable

Figure 6 represents uptake curves for three column studies (Columns J, K, and L), in which the influent concentration of sulfonated alkylbenzene was the only variable. The flow rate for each experiment was 2.5 gpm/ft^2 and each column contained 45 grams of 0.273-mm Columbia carbon.

The effect of concentration on the total quantity of solute removed from solution by the carbon accords well with that which would be anticipated on the basis of the increased driving force for transfer with increased concentration of solute in solution.

Both the mass transfer rate and the total quantity of solute removed from solution at any period of time increase with increasing influent concentration. The mass transfer rate for the experiment in which the influent concentration of solute was 73.3 μmols per liter has a value of 4.28 μmol per gram-hour while the rate for a 13.2 μmol per liter influent concentration is 0.81 μmol per gram-hour. After 100 hours of operation, the carbon in the experiment in which C_o = 73.3 μmol per liter had removed a total quantity of solute equal to approximately 11% of the weight of the adsorbent, and for the study with C_o = 13.2 μmol per liter the solute removed after the same period was barely 3% of the weight of the carbon.

It is again of interest to note that with increasing influent concentration the linear segment of the solute uptake curve extends over a shorter period of time; i.e. film diffusion remains rate limiting for shorter periods of time. This observation is in direct accord with the consideration that film diffusion controls as the rate-limiting step to the point at which the external surface area becomes essentially saturated. The greater the influent concentration of the solute the more rapidly the external surface area becomes saturated, thereby yielding shorter periods over which film diffusion is rate controlling.

Mass transfer coefficients for different influent concentrations of solute have been found to be essentially equal over the range of influent concentrations studied. Equation 2 shows that the mass transfer rate is equivalent to the product of the mass transfer coefficient, the surface area and the influent concentration. Since the transfer coefficient and the surface area, were constant for different influent concentrations in the present column studies, it is to be expected, on the basis of the mathematical model, that the transfer rate should vary linearly with the influent concentration. This theoretical linear variation of transfer rate with initial concentration is adequately confirmed by the experimental data. Based upon the mass transfer rate for Column J ($4.28 \frac{\mu mols}{g - hr}$) in which the influent concentration was 73.3 μmols/liter, mass transfer rates of 0.77 μmols/g-hr and 2.3 μmols/g-hr would be expected on the basis of linear proportionality for influent concentrations of 13.2 μmols/liter and 39.4 μmols/liter respectively; the corresponding measured values were 0.81 μmols/g-hr and 2.2 μmols/g-hr. This agreement between the experimental data and the predictions from the mathematical model provide confirmation of the validity of the latter.

pH as a Variable

To determine the effect of solution pH on mass transfer rates, four experiments (Columns N, O, P, and Q) were conducted at different pH values, each with a column containing 45 grams of 0.273-mm Columbia carbon and operated at a flow-rate of 2.5 gpm/ft^2. The initial concentration of sulfonated alkylbenzene in each experiment was in the range of 79 to 81 μmols per liter. Adjustment of pH in the solutions to values of 3.9, 6.6, 7.9, and 10.0, respectively, was accomplished by appropriate addition of phosphoric acid - phosphate buffers. The pH values given are for the influents to the columns.

Data for the pH studies are presented in Figure 7, in which total quantity of solute removed from solution is represented as a function of time. There is a notable difference between the total quantities of solute removed from solution in the experiments at the highest and lowest pH values tested, the total amount at any time being considerably greater at lower pH. A very slight dependence of the transfer rate and transfer coefficient on pH is observed in the early stages of the runs where film diffusion is rate limiting. At a pH of 3.9 the transfer rate has a value of 4.9 μmols per gram-hour while at a pH of 10.0 the rate drops slightly to 4.33 μmols per gram-hour. However, in later stages of the runs, where intraparticle transport exerts more influence on the overall rate of uptake, a much more marked dependence of transfer rate on pH is to be noted. For this secondary stage the transfer rate for pH = 3.9 is 1.47 μmols per gram-hour in contrast to a rate of 0.45 μmols per gram-hour at pH = 10.0. The experiments at intermediate pH levels agree well with the observed pattern of pH dependence.

The observed influence of pH can be explained at least qualitatively. It has long been recognized that active carbon surfaces carry a net charge, largely due to various functional groups at the surface. Also, it has been reported that carbon surfaces take up hydrogen or hydroxide ions from solution phase, the preference of the surface for one of these two ions over the other being dependent upon the base material, method of preparation, and initial ion concentration.(9) It should be expected that uptake of either hydrogen or hydroxide ions will alter the charge characteristics of the carbon surfaces. When film diffusion is rate limiting during initial stages of column operation, uptake is relatively independent of hydrogen ion concentration as surface charge does not greatly affect film diffusion. However, during later stages of a column run, when pore diffusion becomes rate determining, it should be expected that uptake will be much more dependent on hydrogen ion concentration because the charge characteristics of the surfaces lining the inner pore spaces become important in determining resistance to diffusion of solute molecules through these pores. The observed pattern of dependence of solute removal on pH for the present column studies also accords well with previous work in which both rates and final positions of equilibrium for adsorption of sulfonated alkylbenzenes on the experimental carbon in rapidly mixed batch-type systems were found to increase with decreasing pH.(1,2) The effects noted in the previous work were more pronounced since intraparticle transport was rate limiting over the entire course of the runs in the batch systems.

Temperature as a Variable

Three experiments (Columns R, S, and T) were run at different solution temperatures of 36°C, 28°C, and 16°C. Flow rates of 2.5 gpm/ft^2 were maintained in columns containing 45 grams of 0.273-mm Columbia LC carbon. Initial concentrations of sulfonated alkylbenzene were closely the same for all three experiments, in the range of 77-80 μmols per liter. The experiment at 28°C was at room temperature; for the experiment at 16°C the influent was chilled by immersing a cooling coil in the constant-head tank; a blade-type heater was used in the constant-head tank to heat the influent for the experiment at 36°C. Each temperature given is an average of the influent and effluent for a particular column. Temperature differences between the influent and effluent for each experiment were less than 3°C.

Figure 8 illustrates that there is little difference in rates of uptake for any of the temperatures studied. Consequently the mass transfer coefficients are also essentially equal. Unfortunately, these columns were not carried to the stage at which film diffusion would have ceased to be rate determining. It would be expected, however, the had the studies been continued into the region where pore diffusion became rate limiting, temperature effects would have become more pronounced, similar to the manner in which pH effects were much more marked in the intraparticle transport region than in the film diffusion region. This expectation is based upon observed activation energies for both film and pore diffusion.(10) Activation energies for film diffusion are generally considered to be less than 1 kcal per gram-mole while energies of activation for intraparticle diffusion are likely to be higher than this value.(1,10) Hence, mass transfer rates for intraparticle transport rate control would be expected to exhibit a greater sensitivity to temperature differences than would those for film diffusion control.

Self Regeneration of Active Carbon

In a previous study it had been noted that active carbon appeared to regain some of its "initial ability" for rate of uptake of solute in batch systems during periods it was allowed to stand or rest out of solution.(1) It was assumed that this phenomenon occurred as a result of continued transport of solute within the pores of the carbon during the period it was held out of solution. To further test this behavior for columnar operation, the carbon from Column J was removed from the column at the end of the study, dried at 105°C for 48 hours, and stored at room temperature for two weeks. After drying the carbon plus adsorbed material weighed 52.1 grams, as compared to the initial charge of 45 grams of fresh carbon. The carbon was then replaced in a column and a solution containing 77.1 μmols per liter of sulfonated alkylbenzene was passed through it at a rate of 2.2 gpm/ft^2 (Column M).

The carbon apparently had regained some of its "initial capacity" in that it had a secondary ultimate uptake of approximately 60 μmols per gram as compared to a primary ultimate uptake of greater than 400 μmols per gram of carbon. Thus, in contrast, the secondary capacity was rather limited. The mass transfer rate for secondary uptake was 3.20 μmols per gram-hour as compared to the primary rate of 4.28 μmols per gram-hour.

Multi-Component Competitive Studies

Experiments have been carried out on solute mixtures of three and four components to explore the nature and extent of competitive interactions in continuous flow systems. Such studies have utility for evaluation of the suitability of continuous flow adsorption systems for wastewater treatment, since wastewaters are more often than not heterogeneous mixtures of complex organic compounds of different chemical types and classes.

Three-Component System - To determine the effects of solute interactions on adsorption from solutions containing mixtures of organic compounds, an experimental column was run with a solution containing three different classes of compounds. The influent solution consisted of sulfonated alkylbenzene (ABS) at a concentration of 43.6 μmols per liter, 2-*sec*-butyl-4,6-dinitrophenol (DNOSBP) at a concentration of 31.8 μmols per liter, and quinine sulfate at a concentration of 26.9 μmols per liter as the quinine base. The column contained 45 grams of 0.273 mm Columbia carbon and the flow rate was maintained at 2.5 gpm/ft^2.

Figure 9 is a plot of the total solute uptake curves for each of the components of the mixture. The relative mass transfer rates and mass transfer coefficients for the three components in single and multiple solute systems are tabulated in Table 2. The data plotted in Figure 9 indicate that the mass transfer rate for the sulfonated alkylbenzene is greater than that for DNOSBP, which in turn is greater than that for the quinine. However, in the region where intraparticle transport is rate controlling the relative order of the magnitude of mass transfer rates is changed. In this region the rate for DNOSBP uptake is greater than the rate of uptake of quinine, which in turn is greater than that for the sulfonated alkylbenzene.

TABLE 2

Mass Transfer Rates and Coefficients for Single- and Multiple-Solute Systems

Solute	Single-Solute Solution		Multi-Solute Solution	
	Transfer Rate $(\frac{\mu\text{-mols}}{g - hr})$	$k \times 10^4$ $(\frac{cm}{hr})$	Transfer Rate $(\frac{\mu\text{-mols}}{g - hr})$	$k \times 10^4$ $(\frac{cm}{hr})$
ABS	2.25	1.09	2.82	1.48
Quinine	-	-	1.24	1.43
DNOSBP	2.04	1.42	2.08	1.48

Examination of the experimental values listed in Table 2 for the transfer rates and coefficients for ABS and DNOSBP reveals that there are no appreciable differences in the magnitudes of these parameters between single-solute and multi-solute solutions. This experimental evidence supports the assumption that film diffusion is rate determining during the initial stages of a column study, for this assumption leads to the conclusion that completitive solute effects will not greatly affect individual initial transfer rates. Film diffusion of a particular solute occurs primarily in response to the concentration gradient of that solute across the film, and the type of molecule and resultant steric influences should be of minor relative import during this phase of uptake from solution. This deduction is supported by the fact that the experimental mass transfer coefficients for the various solutes of the multi-component solution are essentially equal. Since the mass transfer rate for any component is equal to $k\ S\ C_o$, and since k and S are constant for any given particle size of carbon, it is readily apparent that the initial transfer rate is directly proportional to the influent concentration for any adsorbing solute, independent of the nature of the adsorbate.

It is to be expected, however, that competitive effects would become pronounced in those later stages of a run during which intraparticle transport limited the overall rate of uptake, since pore diffusion is markedly more sensitive to steric influences.(1) The experimental data confirm this point. Pore-diffusion region transfer rates taken from the data plotted in Figure 9 are 0.67, 0.26, and 0.55 μmols per gram-hour for DNOSBP, ABS, and quinine, respectively. These transfer rates are no longer proportional to the respective influent concentrations, indicating that strict, unhindered diffusion is no longer a predominant rate step. Unfortunately, the single-solute rate studies on the ABS and DNOSBP were not carried to the point at which internal diffusion became rate limiting. Hence, no direct comparison can be made between the single-solute and multiple-solute systems for this region.

Four-Component System - Another column study was conducted with a solution containing four different classes of organic compounds. In this study a coal-base carbon (Pittsburgh SGL) was used instead of Columbia carbon, which had been utilized in all previous studies.

A multiple-component solution containing 24.5 mg per liter ABS, 15.5 mg organic carbon per liter as triethanolamine (TEA) 16.9 mg per liter 2,4-dichlorophenol (2,4-DCP), and 53.7 mg organic carbon per liter as nonylphenoxypolyethoxyethanol (9N10) was passed upward through a one-inch column containing 200 grams of 0.273-mm Pittsburgh carbon, at a flow rate of 2.5 gpm/ft^2. In addition to routine determinations for total organic carbon, ABS, and 2,4-DCP in the effluent solution from the column, several 20-liter samples of the effluent were concentrated by vacuum distillation and analyzed by infrared spectrophotometry.

Figure 10 is a plot of data for the uptake of organic material by the Pittsburgh carbon during this experiment. The data have been plotted in terms of organic carbon removed from solution as a function of time. It was possible, as illustrated in Figure 10, to account for the fractions of organic carbon existing as ABS and 2,4-DCP because these materials were individually determined. Although one fraction is represented as being composed of TEA plus

9N10, the infrared analyses showed complete uptake of 9N10 with considerable leakage of TEA.

TABLE 3

Mass Transfer Rates and Coefficients for a Four Component System

Component	C_O, (mg/l as Organic Carbon)	Mass Transfer Rate, (mg organic carbon/g-hr)	$k \times 10^4$, $(\frac{cm}{hr})$
Total Organic Carbon	91.9	1.18	0.309
TEA & 9N10	69.2	0.68	0.218
ABS	15.2	0.34	0.496
2,4-DCP	7.5	0.17	0.503

Comparison of rates and coefficients listed in Table 3 with those in Table 2 shows that the magnitudes for the mass transfer rates and coefficients for uptake by Pittsburgh carbon in the four-component system are considerably lower than those for uptake by Columbia carbon in the three-component system. This comparison in itself is somewhat misleading, and does not concur with other observations of relative rates of uptake of organic materials from solution by these particular carbons. For example, a transfer coefficient of 1.76×10^{-4} cm/hour obtains for previously published data for adsorption of sulfonated alkylbenzene from a 79.4 μmolar solution in a column containing 61 grams of 0.200-mm carbon operated at a flow rate of 2.5 gpm per sq.ft.(3) In a comparable system with Columbia LC carbon as the adsorbent the mass transfer coefficient had a value of 1.07×10^{-4} cm/hr; considerably lower than that for

Pittsburgh carbon. Further, in previous studies of adsorption of sulfonated alkylbenzenes in batch systems Pittsburgh carbon was found to exhibit a rate constant for adsorption approximately five times as large as that for Columbia carbon of the same particle size.(1) In this present competitive study it is quite possible that the nonylphenoxypolyethoxyethanol, being extremely large in molecular size relative to the other components, in some manner interferes with film transport and hinders the rates of uptake of the other solutes. Nevertheless, the transfer coefficients for ABS and 2,4-DCP are approximately equal in the four-component system as would be predicted on the basis of observations of relative transfer coefficients for the three-component system. The combined transfer coefficient for TEA and 9N10 is considerably lower than those for ABS and 2,4-DCP, largely because of the high leakage of TEA.

The leakage of TEA indicates that some selectivity on the part of active carbon for removal of pollutants will be experienced in practice, and provides some very preliminary indication of the types of compounds that may not be effectively removed by this adsorbent.

SUMMARY

An initial approach has been made toward characterization of rates of uptake of persistent organic pollutants from aqueous solution by active carbon in fluid-bed systems. This work has been directed toward elucidating effects of systemic variables of import in water and wastewater treatment on rates of transfer of pollutants from solution phase to adsorbed phase in both pure and mixed solu-

tions. An elementary, but useful, model for transfer has been utilized for quantifying the relative effects of these variables in terms of mass transfer rates and coefficients.

Rather strong evidence has been obtained to support a conclusion that an extraparticle film-diffusion rate step controls the overall transfer of solute to the porous carbon during initial stages of fluid-column operation. A gradual transition to intraparticle transport as the rate limiting step occurs as the operation proceeds into later stages.

Definite correlation between transfer rate and influent flow rate has been explained on the basis of decreased film thickness at the external solution-solid interface with increased relative velocity between solution and adsorbent particle. At higher flow rates film diffusion has been found to remain rate limiting for shorter periods of time, in accord with expected behavior for the postulated model.

Mass transfer rates for five different sizes of adsorbent particles have been found to be identical; while the mass transfer coefficients for these different sizes have been found to correlate well with external surface area per unit mass of adsorbent. Further, film diffusion remains rate limiting for longer periods for smaller particles. This observation also leads to the conclusion that intraparticle transport does not begin to limit overall rate until such time as the external surface area - which of course increases with decreasing particle size for a given weight of adsorbent - becomes essentially saturated.

Mass transfer coefficients for different influent solute concentrations have been found to be nearly equal over the range of influent concentrations studied. Therefore, for any given size of carbon the transfer rate varies directly as the influent concentration. Also, it has been observed that film diffusion is rate limiting for shorter periods at higher influent concentrations, due to more rapid saturation of the external surface area.

A very slight dependence of transfer rate on the pH of the influent solution has been noted for initial stages of operation. However, transfer rates for those regions of operation in which pore diffusion is rate limiting have been found to increase with decreasing pH. Temperature variation, as well, has been noted to have only a slight effect on transfer rate during the initial stages of a column study. Greater variation is to be anticipated for operation in regions where pore transport is rate determining.

In a three-solute competitive study with substances of roughly similar molecular size initial individual transfer coefficients for each of the three solutes have been found to be essentially equal. For this mixture of compounds the initial mass transfer rate for each solute varies directly as the influent concentration of that solute and is apparently not affected by competitive interactions. Further, the transfer coefficient for a given component of the mixture is very nearly equal to that which obtains for adsorption from a pure solution of the same initial concentration. This apparent independence of transfer rate on the presence of other adsorbates does not hold however for later stages of operation in which intraparticle transport limits overall rate of uptake, since steric effects are of some consequence for rates of pore transport.

Finally, a four-solute competitive study in which one of the components - nonylphenoxypolyethoxyethanol - was of considerably larger molecular size than the other three has indicated that interference with even initial transfer rates can be effected by certain types of materials likely to be found in many wastewaters.

ACKNOWLEDGEMENTS

The work reported herein has been supported in part by research grant WP00706 from the Division of Water Supply and Pollution Control, United States Public Health Service and in part by a Federal Water Pollution Control Administration Research Fellowship Award, number 5-F1-WP-24,505-02 to Mr. T.M. Keinath.

NOTATION

C	Concentration of solute in effluent from column, $\frac{\mu mols}{l}$
C_o	Concentration of solute in influent to column, $\frac{\mu mols}{l}$
C_s	Solute concentration at liquid surface side of interfacial film, $\frac{\mu mol}{l}$
$\bar{C}$	Concentration of solute at solid surface side of interfacial film
k	Mass transfer coefficient, $\frac{cm}{hr}$
m	Mass of adsorbent in column, grams
$N_{Re'}$	Modified Reynolds number, dimensionless
S	External surface area per unit mass of adsorbent, $\frac{cm^2}{gram}$
t	Time, hours
T	Temperature, degrees centigrade

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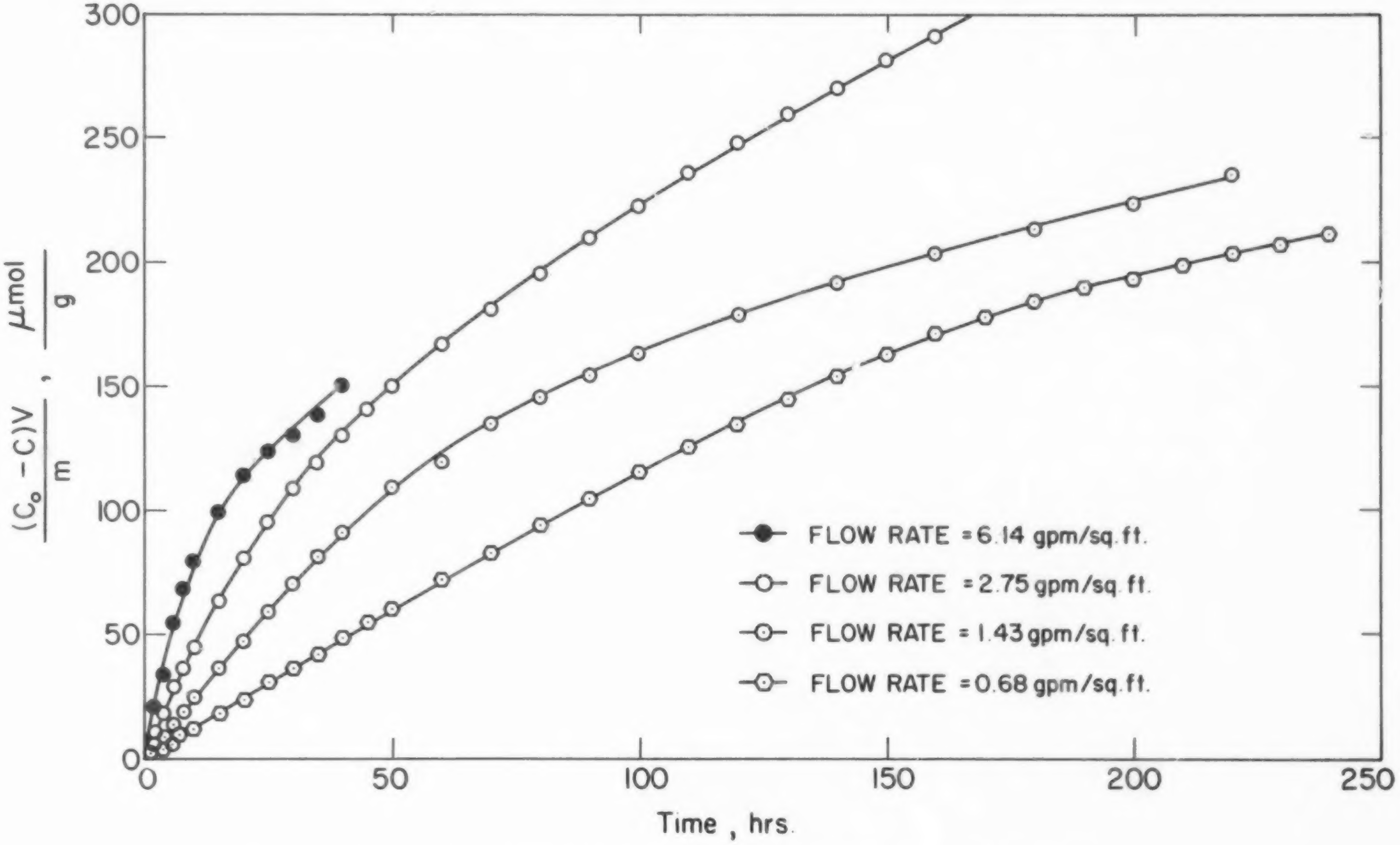

Figure 1. CUMULATIVE ADSORPTION FOR DIFFERENT FLOW RATES

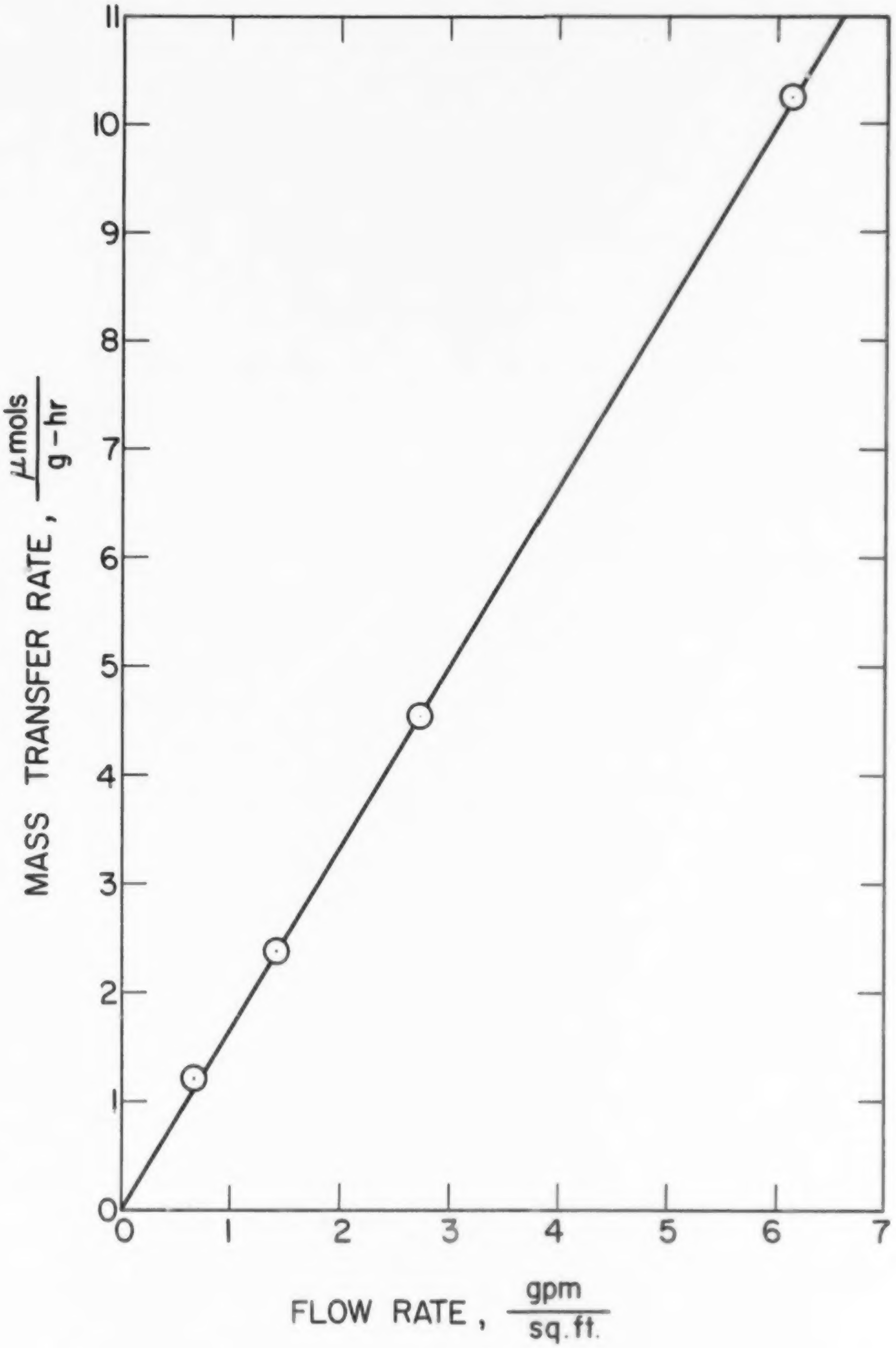

Figure 2. MASS TRANSFER RATE AS A FUNCTION OF FLOW RATE

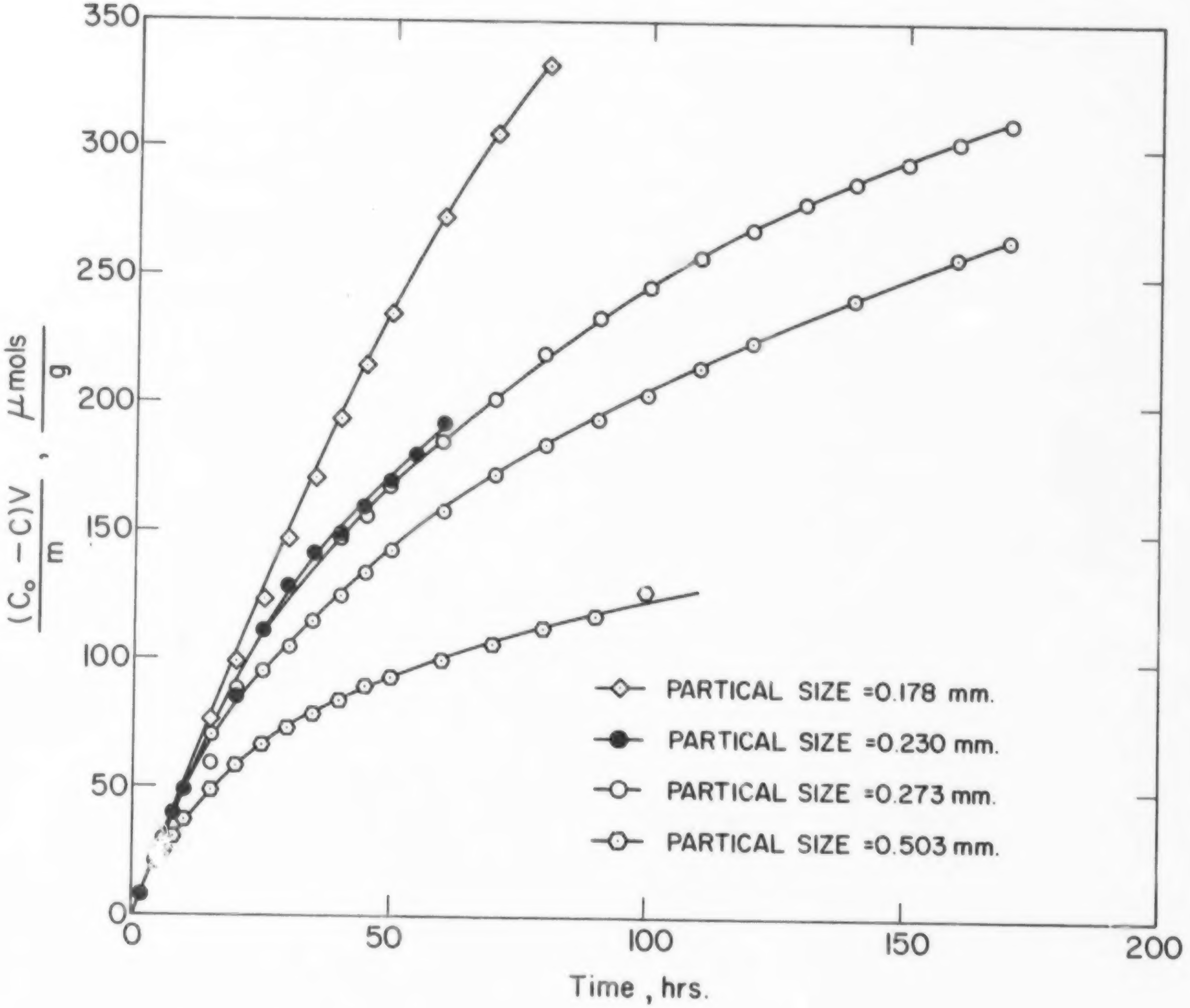

Figure 3. CUMULATIVE ADSORPTION FOR DIFFERENT PARTICLE SIZES

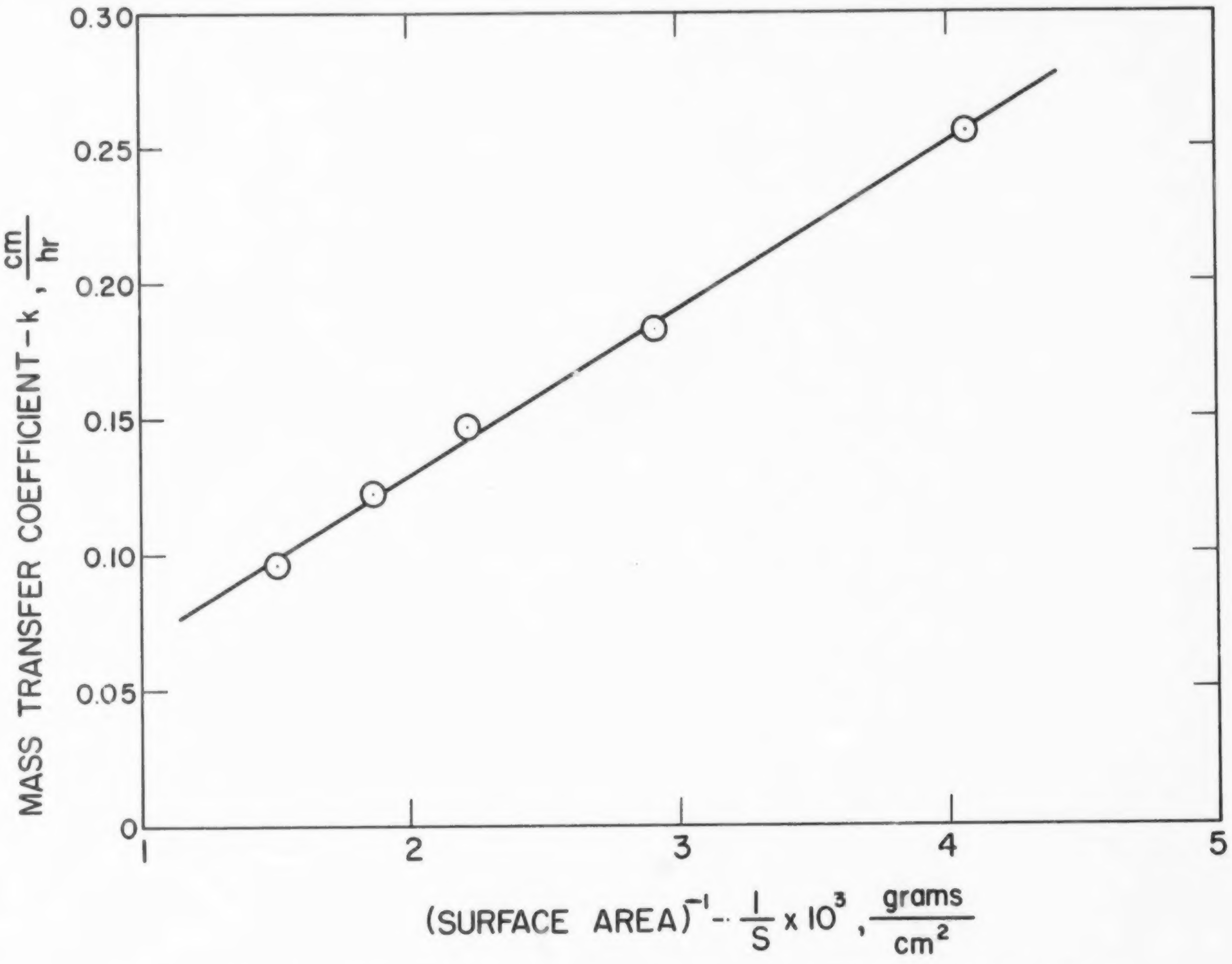

Figure 4. MASS TRANSFER COEFFICIENT AS A FUNCTION OF SURFACE AREA

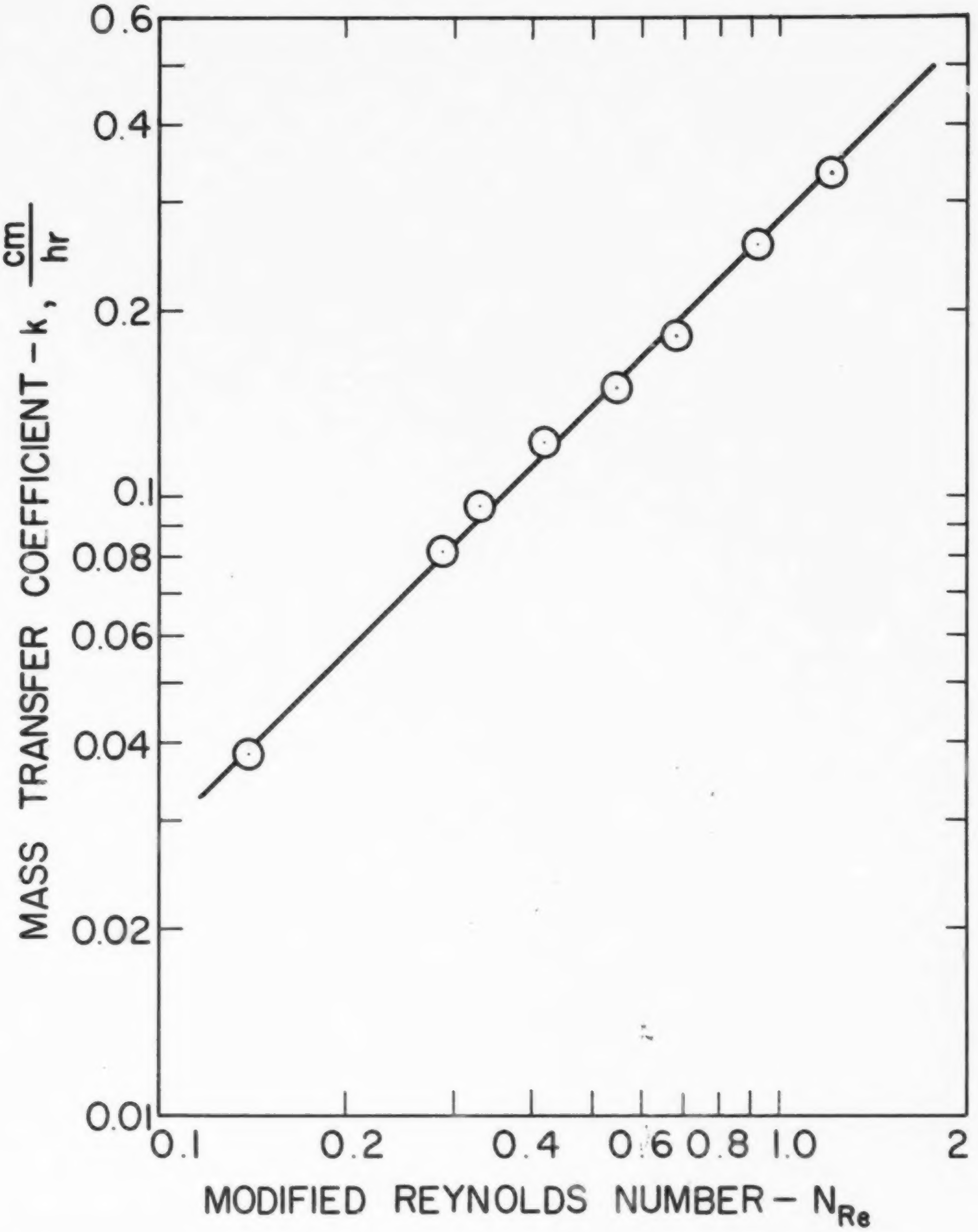

Figure 5. CORRELATION OF MASS TRANSFER COEFFICIENT WITH REYNOLDS NUMBER

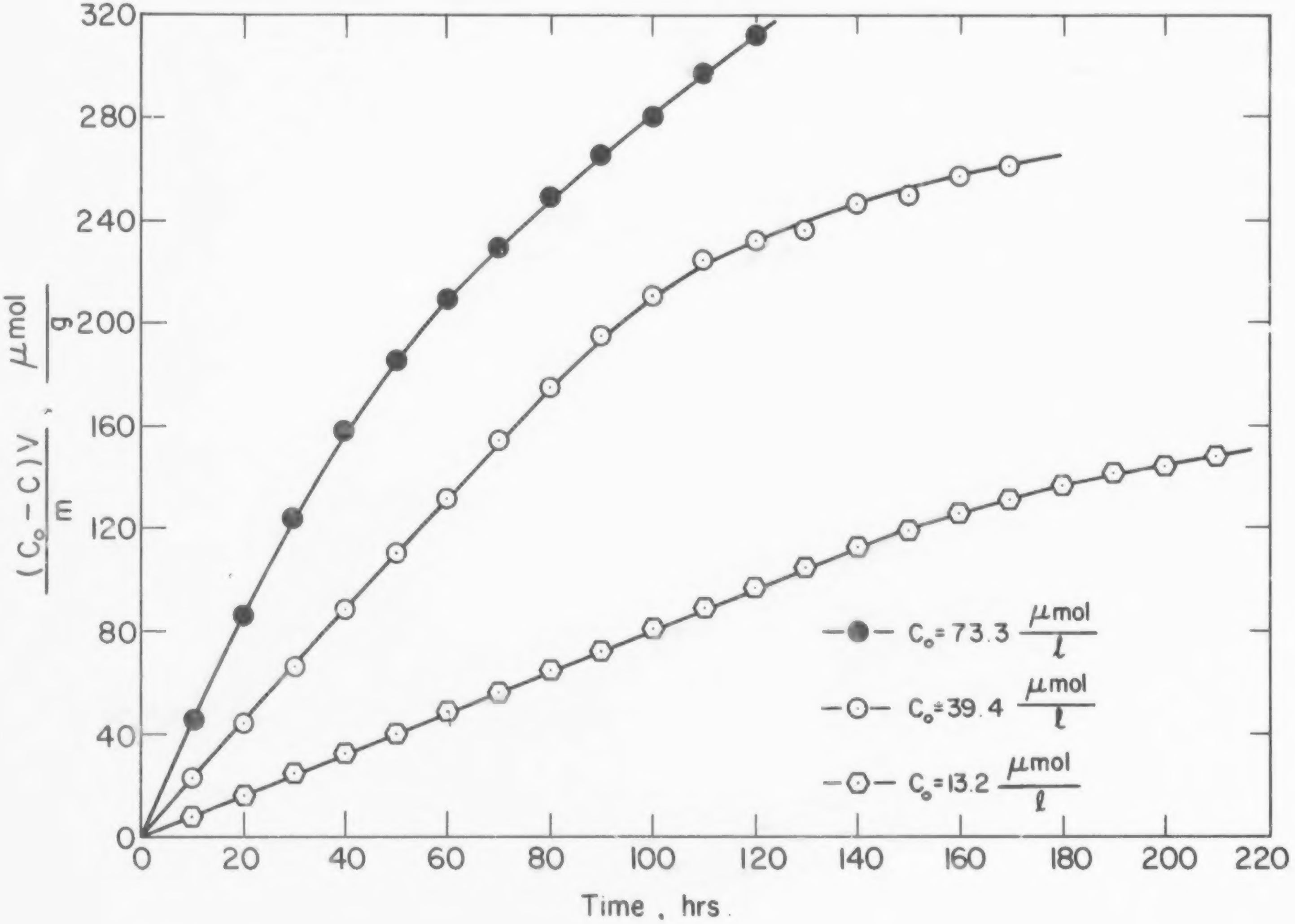

Figure 6. CUMULATIVE ADSORPTION FROM SOLUTIONS OF DIFFERENT CONCENTRATIONS

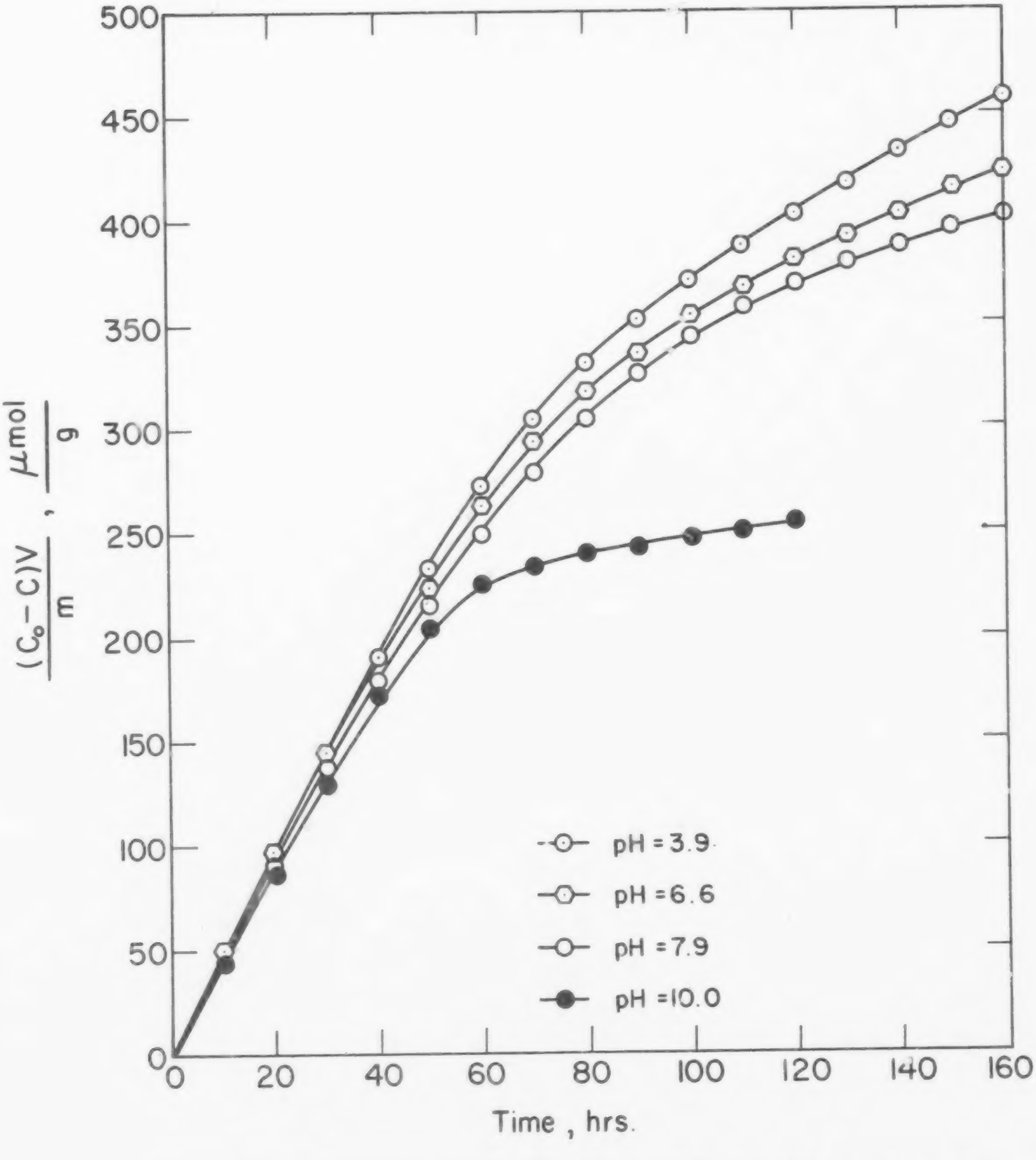

Figure 7. CUMULATIVE ADSORPTION FROM SOLUTIONS OF DIFFERENT pH

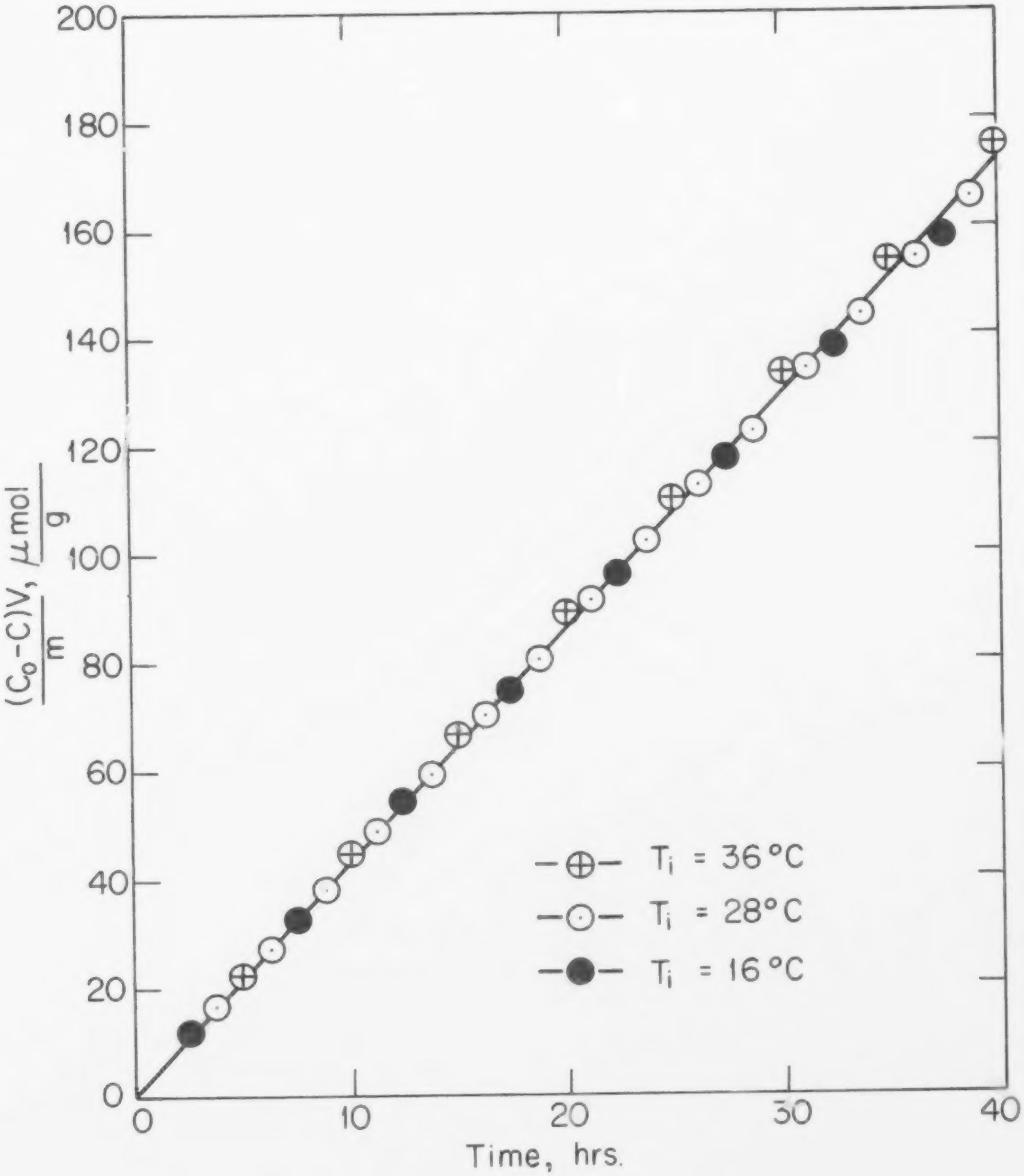

Figure 8. CUMULATIVE ADSORPTION FROM SOLUTIONS AT DIFFERENT TEMPERATURES

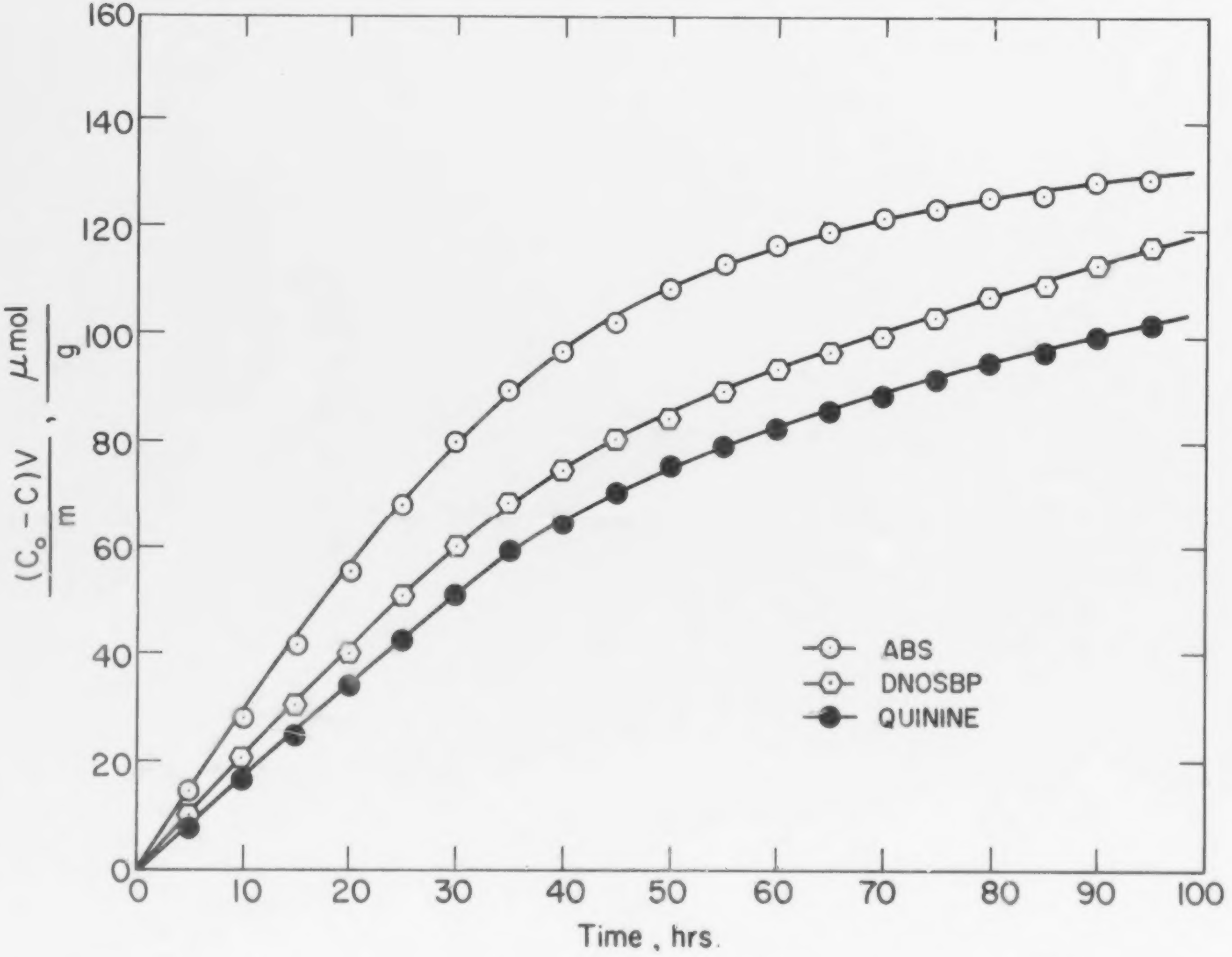

Figure 9. COMPONENT CUMULATIVE ADSORPTION FROM A THREE-SOLUTE MIXTURE

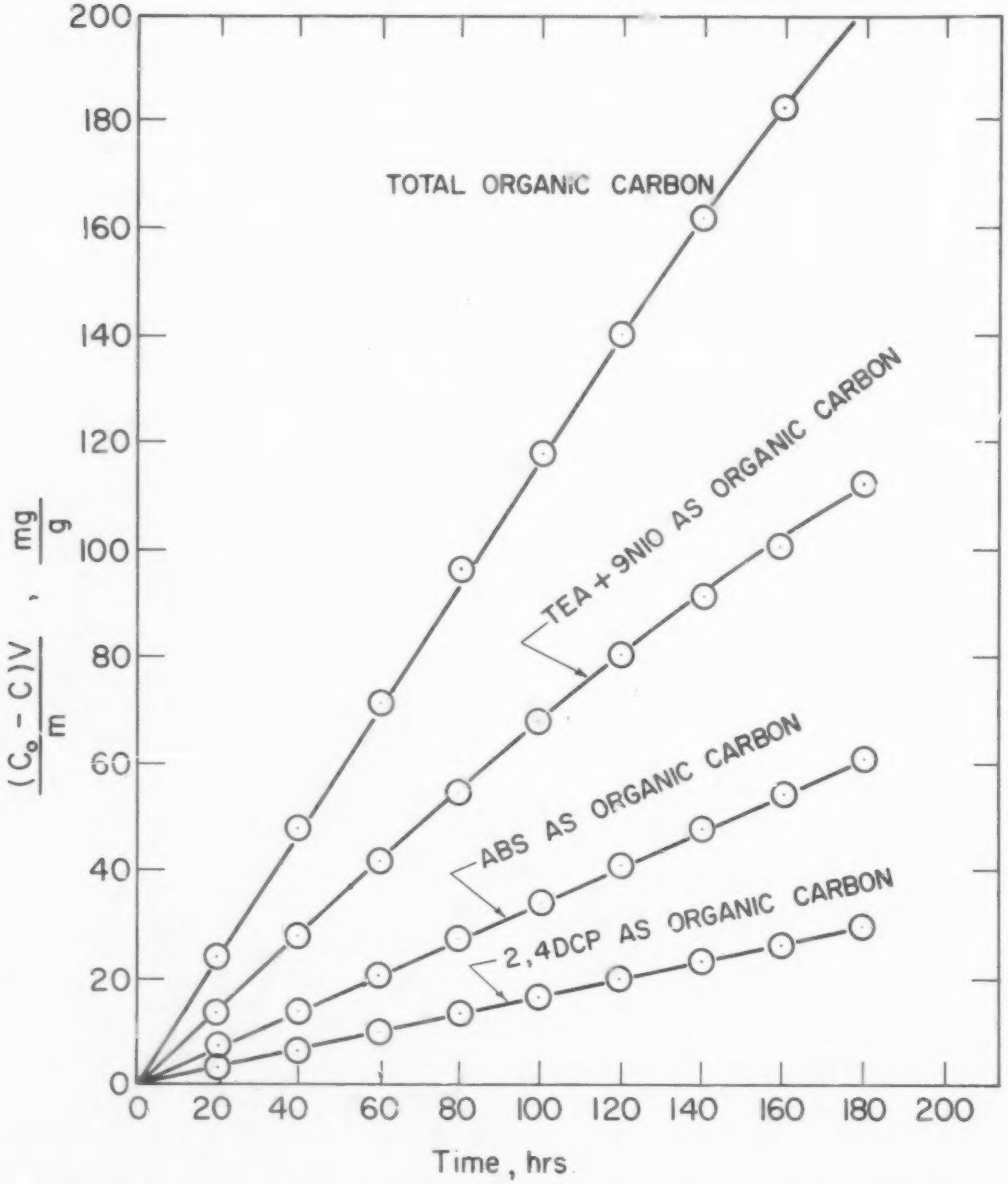

Figure 10. COMPONENT CUMULATIVE ADSORPTION FROM A FOUR-SOLUTE MIXTURE

Prepublication Manuscript

Not for Citation or General Distribution

SORPTION OF ORGANIC PESTICIDES FROM AQUEOUS SOLUTION*

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*Paper presented at the Division of Water, Air, and Waste Chemistry Symposium on Detection, Fate and Effects of Organic Pesticides in Environment, American Chemical Society, Atlantic City, New Jersey, Sept. 1965 (to be published in Advances in Chemistry Series).

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Dispersal of organic pesticides in the environment has been a matter of much recent and widespread concern. One significant aspect of the increased use of pesticides in agricultural, domestic, and industrial applications has been the consequent increase in the occurrence of these materials in waters which receive residue-containing wastes or land drainage. When such waters serve as drinking-water supplies or for recreational purposes, the presence of pesticide materials represents a potential hazard for the health and well-being of the general public. Evidence of the magnitude of the problem may be found in annual production figures; for example, during the one-year period ending in December, 1962, in excess of 350,000 tons of organic pesticides were produced.(7)

If present trends toward increased use of pesticides and related compounds continues, it is quite possible that quantities of these materials reaching our natural water courses may become large enough to represent a potential health hazard in the near future. Further, one must consider the possibility of cumulative toxicity even at current levels of concentration in ground and surface waters. These considerations make urgent the need for development of methods for extracting pesticide materials from waters and wastewaters. In any consideration of treatment methods, the considerable stability of most synthetic organic pesticides must be recognized. Chlorinated hydrocarbons, the most stable class of pesticides, may remain essentially unchanged in a natural water for years. For other classes of pesticides, such as the organic phosphate compounds, partial decomposition may often yield substances (e.g. paraoxon of Parathion) of greater toxicity than the parent compounds.

As might be deduced from their chemical properties, most synthetic organic pesticides are quite resistant to conventional biological treatment. Other conventional water and waste treatment operations are also generally ineffective for removal of pesticides. Coagulation and filtration, for example, are of variable effectiveness, and thus unreliable.(6) Various oxidizing agents, including chlorine, permanganate, chlorine dioxide, and ozone, exhibit some quantitative differences in their respective abilities to oxidize pesticides but are qualitatively similar in behavior.(6) In general, the chlorinated hydrocarbons are affected little by chemical oxidants, and the organic phosphates are converted in varying degrees to oxidation products which may be of greater toxicity than the precursor.

Adsorption on carbon has attracted considerable attention as a possible alternative method for treatment of water and wastewater for removal of organic pesticides. Active carbon has long been known as an effective adsorbent for slightly soluble ring-type compounds, and several studies have indicated that the sparingly soluble cyclic pesticides are no exception. Studies by Hydshaw on adsorption of a number of chlorinated hydrocarbons, chlorophenoxyacetic acids, and organophosphates have demonstrated reductions of 90% or more in pesticide concentrations, for initial concentrations in the range of 50 ppm and lower, with carbon dosages of 20 ppm and less.(4) Aly and Faust have reported capacities for powdered carbon ranging from about 10%-by-weight for the free acid form of 2,4-dichlorophenoxyacetic acid to about 25%-by-weight for the isopropyl ester.(1) Cohen *et al* have indicated similar degrees of adsorption for the fish poisons, Toxaphene and Rotanone.(2)

Objectives of the present studies have been to investigate the adsorption of several of the important classes of organic pesticides and to establish precise physical and thermodynamic parameters. An effort has been made to shed some light on the relatively neglected question of rates of adsorption of pesticides. Further, initial attempts at correlating chemical structure with rate and capacity for adsorption have been made.

As illustrated in Table I, the chemical classes represented by the pesticides studied include thiophosphates (0,0-diethyl-0-p-nitrophenyl phosphorothioate), carbamates (1-naphthyl N-methylcarbamate), dinitrophenols (2,4-dinitro-o-sec-butylphenol and 2,4-dinitro-o-cyclohexylphenol), and chlorophenoxy acids (2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, and 2-(2,4,5-trichlorophenoxy)propionic acid). In addition, a number of molecularly related nitrophenols have been studied for purposes of establishing the effects of molecular geometry and substituent groups on adsorption of pesticide-type materials.

The 0,0-diethyl-0-p-nitrophenyl phosphorothioate (PARATHION) was obtained from the American Cyanamid Company, and the 1-naphthyl-N-methylcarbamate (SEVIN) from the R.A. Taft Sanitary Engineering Center, U.S. Public Health Service. The Dow Chemical Company provided, 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), 2-(2,4,5-trichlorophenoxy) propionic acid (SILVEX), 2,4-dinitro-o-sec-butylphenol (DNOSBP), and 2,4-dinitro-o-cyclohexylphenol (DNOCHP). The 2,6-dinitro-p-cyclohexylphenol (DNPCHP) was obtained from the Mallinckrodt Laboratories, Harvard University; the 2,4-dinitro-thymol (DNT) from Eastman Chemical Products, Inc.; and the 4-nitrophenol (PNP), 2,4-dinitrophenol (DNP), and 2,4-dinitro-o-cresol from the Matheson Company. All compounds as obtained were described by the suppliers as being chemically "pure" relative to the active chemical agent.

Columbia LC carbon, a coconut carbon with high resistance to attrition, was used as the adsorbent in all experiments.(8) Prior to experimentation, the adsorbent was separated by thorough sieving into uniform particle sizes, after which portions of suitable size-range were washed in distilled water to remove leachable impurities and adherent powder, and dried at 105°C. The size-range chosen for the present studies included those particles passing a U.S. Standard Sieve No. 50 and being retained on a No. 60 sieve; the mean particle diameter for this size range is 273 microns. All studies were conducted with carbon from the same manufacturer's lot in order to avoid batch to batch variations.

To eliminate from the experimental systems all extraneous material which might have introduced sources of error and interference, all solutions used in the experimental systems were prepared with twice-distilled water. Tap water was first distilled in a conventional tin-lined still, and the condensate was transferred into an all-glass still for redistillation. Preliminary boiling with escape of steam was used to purge the water of dissolved carbon dioxide and chlorine prior to collection of the condensate from the redistillation.

EXPERIMENTAL DETAILS

Analytical Methods

Of the substances investigated, only PARATHION does not exhibit a characteristic absorption spectrum suitable for direct measurement of concentration within the ranges used in the present experiments. Spectrophotometric data for the other pesticides and related dinitrophenols are listed in Table II.

The analytical method employed for PARATHION takes advantage of the ease with which the phosphorous-oxygen bond in that material is cleaved by hydroxide. The hydrolysis produces a mole of 4-nitrophenol for each mole of PARATHION originally present in solution. Because 4-nitrophenol has a well-defined absorption spectrum with a high molar absorptivity at the wavelength of maximum absorption (400 mμ), and because the reaction to form 4-nitrophenol from PARATHION is rapid and quantitative, the method provides a reliable and sensitive means for analysis of PARATHION.

For fairly concentrated samples (1-100 μM), about 10 ml of 1 N KOH were added to 50 ml of sample. The mixture was refluxed for one hour, allowed to cool, diluted to 100 ml, and then the absorbance at 400 mμ was measured in a cell of appropriate length. For more dilute samples, 3 KOH pellets were added to a 100-ml sample and the procedure outlined above was repeated. The lower limit of the method is about 50 nanomoles/l using a 10-cm cell.

After measurement of the absorption spectrum for each solute had been made with a Beckman Model DK-2 spectrophotometer, the absorption maximum for solutions of each of the substances was located precisely with a Beckman Model DU spectrophotometer by measuring intensities of absorption for a localized region on both sides of the wavelength of maximum absorption indicated by the spectra obtained with the Model DK-2. Subsequent spectrophotometric measurements were made with the Model DU.

Experimental Methods

Agitated non-flow experiments were used for investigating both the kinetics and equilibria of adsorption. The batch technique was selected because of its relative simplicity. Advantages of this type of system include its freedom from complex hydraulic parameters indigenous to flow-through systems, its adaptability to small volume work, ease of investigation of variation of conditions, and general facility of operation.

Although column operation seems likely to be used for large-scale technical applications of carbon adsorption to waste treatment, evaluation of the fundamental characteristics of adsorption is simpler with a batch technique. Furthermore, once suitable functional relationships for the variables have been established, extrapolation of data from batch systems to the prediction of behavior in continuous systems should be feasible.

The reaction vessels for the kinetic studies were 4000-ml resistant-glass bottles, in which solutions were agitated with Teflon-coated stirring rods extending directly into the adsorbate solution and connected to synchronous motors operating at 1550 rpm. Previous kinetic studies in similar systems had shown that rate of adsorption is independent of stirring rate at rotations greater than a few hundred revolutions per minute.(8) Temperature control for the rate studies was maintained by immersing the reaction vessels in water baths, thermo-regulated to ± 0.5°C. All kinetic studies have been conducted at 28°C.

For each experiment on rate of adsorption, an 8-liter volume of adsorbate solution was prepared at a concentration slightly higher than that desired for the kinetic experiment. In order to insure that the nitrophenols studied were present as the anions in the experimental systems, sufficient KOH was added to give a final pH between 9 and 10. Spectrophotometric measurement of the exact concentration of solute in the solution was then made, and the original 8-liter volume diluted appropriately to give more closely a solution of the desired concentration. Exactly 3000 ml of the adjusted solution was then placed in each of two 4-liter reaction vessels. The reaction vessels were then placed in a water-bath for approximately 24 hours to allow the solution to attain the desired temperature and to reach adsorptive equilibrium with the surfaces of the vessels. Prior to introduction of a suitable, accurately weighed quantity of carbon to each vessel, an initial sample was removed and analyzed for concentration of adsorbate. This gave an accurate check on the preparation of the solution and served as the reference concentration for the rate study. The carbon was then introduced into the vessel and was rapidly dispersed by the motor-driven stirrer operating at 1550 rpm. At appropriate intervals the stirring was briefly interrupted while samples of the supernatant solution were pipetted from each of the reaction vessels; the samples for anlysis resulted in some small decrease in total adsorbate available to the adsorbent, but the cumulative error of 2% to 3% was not significant for this type of experiment. The running of two parallel experiments, identical in all details, provided a check on the reproducibility of the data.

For investigation of adsorptive capacities and equilibria, large volumes of adsorbate solution were prepared and 250-ml measures of this solution were dispensed into 300-ml resistant-glass reaction flasks. A suitable, accurately weighed amount of adsorbent was then added to each flask, the weight being varied so as to cover the range of equilibrium solute concentrations of interest. For each study, several flasks of solution were left without carbon for use as blanks. The ground-glass-stoppered reaction flasks were then sealed and placed in an oscillating shaker to be shaken for approximately two weeks, the time required for equilibrium to be obtained having been determined previously for each type of system. Samples from each of the solutions were analyzed at the end of the appropriate period; the amount of adsorption was computed from the difference between the concentration of adsorbate measured for the blanks and for each reacted solution. Most studies were conducted in a room that was maintained at a reasonably uniform temperature, so that fluctuations in the temperatures of the solutions were no more than 2 to 3°C over the duration of the study. The mean temperature for the equilibrium studies was 25°C.

ADSORPTION RATES

Previous investigations have indicated that the rate-limiting step for removal of organic solutes from dilute aqueous solution by porous active carbon in agitated non-flow systems is one of intraparticle transport of the solute in the pores and capillaries of the adsorbent.(10) For systems in which intraparticle transport is the rate-limiting step, data for uptake of solute from solution should give a linear plot as a function of the square-root of time from introduction of the adsorbent to the system.(3) In accord with this method for representing data for systems in which intraparticle transport is the rate-limiting mechanism, the data for the present experiments have been plotted as a function of the square-root of time.

Representative rate data - for 2,4,5-T and PARATHION - for the experiments on adsorption of pesticides on active carbon are presented in Figures 1 and 2. The $(C_o-C)/m$ values in these plots represent the amount of solute, both in micromoles and milligrams, removed from solution per gram of carbon. Good linearization of the data is observed for the experiments, in accord with expected behavior for intraparticle-transport rate control. Similar linearization obtained also for data for the other pesticides. The linear traces facilitate comparison of relative rates of adsorption of pesticides, and such comparison is made in Column 1 of Table III, using the square of the slope of each plot as the relative rate constant for the experiment.

It is of interest that the rate constants for adsorption of the various organic pesticides on the 273-micron carbon are remarkably similar. The data suggest that, even for a rather broad spectrum of different types of organic pesticides, similar rates of removal from solution should obtain. Thus, the effectiveness of active carbon as relates to rate of removal of organic pesticides from solution should be relatively independent of the type of organic pesticide, at least within the classes of compounds and conditions used for the present experiments.

Pesticide Concentration

Concentration of pesticide has been observed in the present experiments to have a significant effect upon rate of removal by active carbon. The rate data listed in Table III are for experiments conducted with a solution containing solute in initial concentration of about 10 μmol/l. Figure 3 illustrates some data for experiments conducted with certain of the pesticides at concentrations greater than and slightly less than 10 μmol/l. The uppermost curve in Figure 3 is for adsorption of 2,4-D from a 52.2- μ*M* solution. The middle curve in Figure 3 is for a 45.2- μ*M* solution of SILVEX, and the lower curve is for adsorption of DNOCHP from a solution with an initial concentration of 7.7 μmol/l.

For 2,4-D the 5.1-fold increase in initial molar concentration resulted in a new rate constant of 16.0×10^4 $(\mu\text{mol/g})^2$/hr as compared to a value of $1.44 \times 10^4 (\mu\text{mol/g})^2$/hr for experiments in which the initial concentration was 10.3 μmol/l. The experiment at high concentration with SILVEX, representing a 4.6-fold increase in initial molar concentration, yielded a new relative rate constant of $7.56 \times 10^4 (\mu\text{mol/g})^2$/hr as compared to a value of $0.71 \times 10^4 (\mu\text{mol/g})^2$/hr for experiments with an initial molar concentration of 9.8 μmol/l.

It is interesting to note that the ratio of the relative rate constants for the two solutes, 2,4-D and SILVEX, obtained from experiments at low concentration is 2.03, while the ratio of the relative rate constants obtained from experiments at high concentration is 2.11. Thus, it appears that the effect of initial concentration upon the rate at which organic pesticides are removed from water by active carbon is relatively uniform, at least for similar classes of organic pesticides.

While the effect of concentration is qualitatively evident, it is essential for purposes of engineering design and operation of adsorption processes that rather precise prediction of concentration or "load" effect be possible. Previous findings relative to the concentration dependence of rate of uptake of certain other pollution materials by active carbon indicate a linear relationship between the relative rate constant expressed in units of μmol/g-hr$^{0.5}$ and the square-root of initial concentration.(8) To evaluate more quantitatively the dependence of rate of adsorption upon initial pesticide concentration, and to test the generality of the conclusions reached in the previous work cited, a series of experiments was performed in which the initial concentration of a selected pesticide, DNOSBP, was varied from 1.1 μmol/l to 96.9 μmol/l. Relative rate constants, expressed in units of $(\mu\text{mol/g})^2$/hr, derived from the present experiments are plotted in Figure 4 versus initial concentration of solute. The linearity of the trace so obtained indicates good agreement with the concentration dependence of adsorption rate noted previously for sulfonated alkylbenzenes.(8) Thus, the previous and present experiments suggest that the nature of the effect of concentration may well be general and quantitatively, as well as qualitatively predictable.

The data plotted in Figure 1 indicate a dependence of the relative rate constant on concentration of 1180 (μmol/g)^2/hr for each μmol/l, or 1180 μmol-l/g^2-hr. Preliminary experiments with initial concentrations of DNOSBP in the nanomolar range suggest reasonably close adherence to this rate dependence even at extremely low concentrations.

Molecularly Related Nitrophenols

In order to define more explicitly the relative influences of molecular structure and hydrophobic character upon rate of adsorption of pesticide materials by porous carbon, a number of pure dinitrophenols, molecularly related to DNOSBP and DNOCHP, have been studied. The molecular structures of DNOSBP, DNOCHP and the molecularly related dinitrophenols - DNP, DNC, DNT, and DNPCHP - are illustrated in Figure 2.

As may be noted in Figure 5, the first four compounds of this series - DNP, DNC, DNOSBP, and DNOCHP - are 2,4-dinitrophenols with various substituent groups in the remaining ortho position. The fifth member of the series - DNT - is a 2,4-dinitrophenol isomeric with the DNOSBP but possessing two alkyl groups rather than one, while the sixth member - DNPCHP - is a dinitrophenol isomeric with the DNOCHP.

Relative rate constants for adsorption of these compounds on the experimental carbon are tabulated in Table III.

Because all six members of the dinitrophenol series were studied as the highly soluble anions, solubility effects can be largely neglected in comparing relative rates of adsorption. Primary considerations then would be hydrophobic character, affecting the rate at which solute transferred from liquid to solid phase, and molecular geometry, affecting rate of intraparticle transport through the influence of steric effects.

One may note from comparison of the relative rate constants listed in Table III that rate of adsorption increases rapidly in the series DNP-DNC-DNOSBP, suggesting that increasing hydrophobic nature increases rate of adsorption over this range more rapidly than the increasing molecular area can act to retard rate. However, in further comparison of the rate constant for DNOSBP with that for the more hydrophobic DNOCHP, one observes a substantial decrease in rate of adsorption, suggesting that the geometric difference between the relatively small and easily deformed sec-butyl group and the larger and comparatively rigid cyclohexyl group is enough to overide the influence of the increase in hydrophobic character. The structure of the sec-butyl group permits bending of carbon-carbon and carbon-hydrogen bonds in such fashion as to permit more rapid migration into the pore structure of the carbon, while such bending or deformation is rather limited for the cyclohexyl group.

In studying the two pairs of isomers, DNOSBP-DNT and DNOCHP-DNPCHP, it is possible to neglect hydrophobic character - which will be largely constant among isomers - and concentrate on molecular geometry. Comparing the structures of DNOSBP and DNT, one may deduce that the DNT molecule with its fairly rigid alkyl groups might present a larger effective cross-sectional area for diffusion than will the DNOSBP with its single and relatively flexible alkyl group. The correctness of this deduction is confirmed in the experimental observation that the rate of adsorption for DNOSBP is twice that for DNT.

An explanation of the observed difference between adsorption rates for DNOCHP and DNPCHP is not as straight forward as for the DNOSBP-DNT isomer pair. One possibility is that the cyclohexyl group is less able to fold out of the way when in the para position than when in the ortho position, thus presenting a less compact form for pore transport. In addition, it is likely that the concentration of three quite inductive groups on adjacent carbon atoms in the DNPCHP molecule tends, through resulting electrostatic interaction with functional groups at the surface of the carbon, to retard transport while in the DNOCHP molecule the spread position of the three inductive groups decreases their influence. A third possibility is that, due to steric interactions, the two nitro groups are forced apart out of the plane of the ring and to opposite sides of it, increasing further the steric hinderence to pore transport.

ADSORPTION EQUILIBRIA

The extent to which the full surface area of an active carbon can be used for adsorption depends on the concentration of solute in the solution with which the carbon is mixed. The specific relationship between concentration of solute and degree of removal from solution, at constant temperature and for conditions of equilibrium, defines the adsorption isotherm. The preferred form for representing the adsorption isotherm is to express the quantity of solute adsorbed per unit weight of adsorbent as a function of C, the equilibrium concentration of solute remaining in solution.

A number of different types of adsorption relationships may obtain under different circumstances. The most common relationship between the amount of solute adsorbed per unit of adsorbent and the equilibrium concentration in solution is obtained for systems in which it appears that adsorption from solution leads to the deposition of only a single layer of solute molecules on the surface of the solid. This type of adsorption equilibrium is best represented by the Langmuir model for adsorption, which assumes that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no movement of adsorbate molecules in the plane of the surface after initial adsorption.(5)

The form of the Langmuir adsorption isotherm is

$$X = \frac{X_m bC}{1 + bC} \text{ ----------------------- } (1)$$

in which C indicates the measured residual concentration in solution at equilibrium, X_m is equal to the number of moles of solute adsorbed by one gram of carbon in forming a complete monolayer on the carbon surface, X represents the number of moles of solute adsorbed per gram of carbon at concentration C, and b denotes a constant related to the energy of adsorption. The reciprocal, 1/b, is the concentration at which adsorption attains half its limiting X_m value.

Two convenient linear forms for the Langmuir equation are:

$$\frac{1}{X} = \frac{1}{X_m} + \frac{1}{bX_mC} \text{ -------------------- } (2)$$

and

$$\frac{C}{X} = \frac{1}{bX_m} + \frac{C}{X_m} \text{ -------------------- } (3)$$

Either Equation 2 or Equation 3 may be used for linearization of data that conform to the Langmuir equation. The form chosen usually depends on the range and spread of the data and on the particular range of data to be emphasized.

All of the organic pesticides tested exhibit equilibrium adsorption on the experimental carbon in reasonable accord with the Langmuir model for adsorption. Representative data for the isothermal equilibrium adsorption experiments are plotted in Figures 8 and 10 for 2,4,5-T and PARATHION, respectively. The points on these plots are the experimental data; the solid curves through the points are calculated Langmuir adsorption isotherms. Figures 3 and 5 are plots of the same data according to the linear form of the Langmuir adsorption isotherm given by Equation 2. The ordinate intercept of the line drawn through the data in each of Figures 3 and 5 represents the reciprocal of the ultimate capacity for adsorption, $\frac{1}{X_m}$, and the slope of each plot represents the reciprocal of bX_m. From the intercepts and slopes of such linear plots, values for the Langmuir constants for each solute have been calculated; these values are listed in Table III.

As was the case for the relative rate constants for the different organic pesticides, values of X_m, listed in Table III, are quite similar in magnitude for the different adsorbates, on the order of 1800 micromoles of solute per gram of carbon. Thus, the ultimate capacity appears to be relatively independent of the type of organic pesticide tested, at least within the experimental ranges. With the exception of the PARATHION, values for the parameter b, which is a measure of the energy of adsorption, are quite similar for the organic pesticides. The fact that the value for b for the PARATHION is an order of magnitude higher than values of b for the other organic pesticides indicates that this material has a high energy of adsorption and attains adsorptive capacities near the ultimate capacity at relatively low equilibrium concentrations.

THERMODYNAMIC CONSTANTS

Equilibrium capacity for adsorption of organic solutes on carbon can be predicted to increase with decreasing temperature, for adsorption reactions are exothermic. The differential heat of adsorption, ΔH, is defined as the total amount of heat evolved in the adsorption of a definite quantity of solute on an adsorbent. Heats of vapor-phase adsorption generally are several thousand calories per mole, but because water must be desorbed from the surface during adsorption from aqueous solution, heat changes tend to be somewhat smaller than for vapor-phase adsorption.

The differential heat of adsorption may be calculated from maximum levels of adsorption at two or more different temperatures and the van't Hoff-Arrhenius equation in the form,

$$H = \frac{RT_1T_2}{T_2 - T_1} (\ln X_{m,1} - \ln X_{m,2}) \text{ ------------ } (4)$$

where R is the Universal Gas Constant, T_1 and T_2 are the absolute temperatures of two otherwise identical systems, and X_m is for this example the limiting monolayer adsorption value for the Langmuir adsorption model. A plot of values for the logarithm of X_m versus the reciprocal of absolute temperature for a given system should then yield a linear trace with a slope equal to $\Delta H/RT_1T_2$.

While the temperature dependence of equilibrium capacity for adsorption is defined by the parameter ΔH, the dependence of rate of adsorption is usually expressed in terms of the activation energy, E. Rate of adsorption is related to the activation energy by the equation,

$$k = Ae^{-E/RT} \text{ ------------------------- } (5)$$

where k is the absolute rate constant, T the absolute temperature and A is a temperature-independent factor sometimes called the frequency factor. Equation 13 may be written

$$\ln k = \ln A - \frac{E}{RT} \text{ --------------------- } (6)$$

which implies a linear relationship between ln k and $\frac{1}{T}$ with a slope of E/R. Equation 6 may be written for any two rates, k_1 and k_2, corresponding to absolute temperatures T_1 and T_2, respectively, and the difference expressed as

$$E = \frac{RT_1T_2}{T_2 - T_1} (\ln k_1 - \ln k_2) \text{ ----------- } (7)$$

which has the same form as Equation 4. From this relationship E can be evaluated for any system in the same fashion as ΔH.

For uptake of solute from solution by porous solids the rate will be endothermic rather than exothermic if intraparticle transport is the rate limiting mechanism. Because diffusion is an endothermic process, while adsorption is exothermic, rate of uptake of solute by porous solids will often increase with increasing temperature while for the same system the equilibrium position of adsorption or adsorption capacity will decrease with increasing temperature.

Plots of the relative rate constants versus T^{-1} for three different classes of the pesticides studied, along with those for the neutral and ionic species of 4-nitrophenol are given in Figure 10, and the corresponding values for the respective energies of activation are listed in Table IV. It should be noted that the activation energies derived from the present experimental data, unlike previous values calculated for sulfonated alkylbenzenes, are based on relative rate constants expressed in units of (micromoles/gram)^2 per hour. It is felt that the thermodynamic constants so calculated are more closely representative of absolute-rate-theory values. In accord with expectations for intraparticle transport as the rate-limiting mechanism, the experimental activation energy values tabulated in Table IV are all positive. Thus the kinetics of uptake of the pesticides by porous carbon is endothermic.

Comparison of the values for E for the various pesticides and the neutral and anionic species of the simple nitrophenol indicates that a much higher activation energy is associated with adsorption of neutral molecules (PARATHION and the neutral nitrophenol) than with adsorption of anions (2,4-D, DNOSBP, and the anionic nitrophenol). This observation suggests the possibility of two different rate-limiting steps in the intraparticle transport mechanism. Current studies are being directed toward more detailed exploration of the observed thermokinetic phenomena.

The effects of temperature on the equilibrium capacity of active carbon for adsorption of 2,4-D and DNOSBP have been studied. The data are plotted in Figure 11 and the experimentally determined heats of adsorption listed in Table IV. The values for ΔH for the 2,4-D and DNOSBP are remarkably similar, and, as one would anticipate from consideration of the thermodynamics of adsorption, both values are negative. In general, however, it may be anticipated that normal temperature variations in practical applications will not significantly affect ultimate capacity for sorption of organic pesticides on carbon.

SUMMARY AND CONCLUSIONS

Comparison may be made between the adsorption capcities, in terms of the Langmuir constants X_m and b, for the organic pesticides and those obtained in previous studies for sulfonated alkylbenzenes and other pollution materials.(9) Results of some of the previous studies along with those from the present investigation are summarized in Table V.

It is apparent from the X_m values listed in Table V that capacities for adsorption of the organic pesticides on active carbon are quite large, greater on a molar basis than phenol and sulfonated 2-dodecylbenzene, and greater on a weight basis than any of the three other compounds. On the other hand, the b^{-1} values, except for PARATHION, indicate approach to saturation adsorption only at relatively high residual concentrations.

By way of comparison of the capacity data derived from the present experiments with capacity data obtained by other investigators for the same solute, a plot of an experimental isotherm presented by Aly and Faust for adsorption of 2,4-D on powdered carbon indicates an adsorption capacity of 80 mg/g corresponding to an residual concentration of 0.5 mg/l.(1) One may calculate from the Langmuir data presented in Table V that the present experiments predict a capacity of 70 mg/g, at the 0.5 mg/l residual concentration level, for adsorption on the comparatively large 273-micron experimental carbon. A considerably higher capacity is to be expected for the very fine carbon used by Aly and Faust, according to previous observations on the effect of particle size on equilibrium capacity.(9) Indeed, one would anticipate a capacity somewhat in excess of 80 mg/g for carbon of the size used by Aly and Faust (95 per cent passing a 325-mesh sieve). However, in light of the differences in carbon type and carbon size, the agreement may be considered rather good.

The capacity figures presented in Table V are probably most significant for column operation, for counter-current operation makes realizable those capacities corresponding to initial concentrations rather than to allowable effluent concentrations. The b^{-1} values give an indication of the anticipated sharpness of the breakthrough front and to some extent provide guidance for the optimum depth of column for satisfactory removal of the contaminant, although rate of adsorption is an equally important factor in this respect. Larger b^{-1} values in general would call for greater depths of adsorption column.

Analysis of this type can give only very qualitative conclusions with regard to the pesticides for it is obvious that the basic assumption of the Langmuir treatment, that only a monomolecular layer of adsorbed material is formed, does not hold when one is considering weights of adsorbed material in the neighborhood of 40% of the weight of adsorbent. While the Langmuir formulation does provide an adequate representation of the data for adsorptive equilibrium over a large and relatively high concentration range, it seems likely that more refined experimentation in a lower concentration range (say 1-100 ppb) would show considerably greater adsorption of the pesticides than that predicted by the Langmuir constants presented here. Indeed experimental results for the lower end of the concentration range for equilibrium adsorption of DNOSBP and DNOCHP, shown in Figure 12 and 13 respectively, provide some evidence of this. It seems likely that two different Langmuir formulations may be needed for more exact description, such as those found for phenol in lower and higher ranges of concentration.(9) There the value of X_m for phenol at higher concentrations was found to be 3.32 mmol/gram or 310 mg/gram rather than the figures recorded in Table V. It is to be noted from the prvious work that the phenol concentrations giving the higher capacity were from 6 to 14% of the saturation values in water. Many of the pesticides were studied in about this range of fractional concentrations of their saturation values. In addition, carbons of particle sizes smaller than the 273-micron carbon utilized for the present work will yield higher adsorption capacity values, as has been demonstrated by Weber and Morris.(9)

Consequently, clean-up of small concentrations of pesticides by activated carbon seems likely to be considerably more efficient than indicated by the Langmuir constants obtained in these studies. Problems of initial leakage of these materials are not expected to occur when beds of adequate depth (5-10') of active carbon are used for water and wastewater treatment.

ACKNOWLEDGEMENTS

The research reported herein has been supported in part by U.S. Public Health Service AWTR Contract SAph 76495 and in part by a Research Grant, WP-00706-01A1, from the Division of Water Supply and Pollution Control, U.S. Public Health Service.

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10. Weber, W.J., Jr., and Rumer, R.R., Jr., "Intraparticle Transport of Sulfonated Alkylbenzenes in a Porous Solid: Diffusion with Nonlinear Adsorption", Water Resources Research, 1, 3, 361 (1965).

FIGURE CAPTIONS AND DESCRIPTIONS

Figure 1. RATE OF ADSORPTION OF 2,4,5-T

Adsorption of 2,4,5-trichlorophenoxyacetic acid on 273-micron Columbia LC carbon. Initial concentration, C_o, is a 9.8 micromoles per liter and the carbon dose, m, is 25 milligrams per liter. Temperature is 28°C. Cumulative uptake of 2,4,5-T per gram of carbon is plotted as a function of the square-root of time for linearization of the data. Uptake is given in terms of micromoles per gram of carbon on the left ordinate and milligrams per gram on the right ordinate.

Figure 2. RATE OF ADSORPTION OF PARATHION

Cumulative uptake of 0,0-diethyl-0-p-nitrophenyl phosphorothioate from a 10.0 μM solution by 25 milligrams per liter 273-micron Columbia LC carbon.

Figure 3. RATES OF ADSORPTION OF 2,4-D, SILVEX, AND DNOCHP FROM SOLUTIONS OF DIFFERENT INITIAL CONCENTRATION

The open circles are for adsorption of 2,4-dichlorophenoxyacetic acid from a 52.2 μM solution; the triangles for 2-(2,4,5-trichlorphenoxy)propionic acid from a 45.2 μM solution; and the solid circles for 2,4-dinitro-o-cyclohexylphenol from a 7.7 μM solution.

Figure 4. EFFECT OF INITIAL CONCENTRATION ON ADSORPTION OF DNOSBP

Rate constants obtained from a number of experiments with different initial concentrations are plotted versus initial concentration to give a linear trace. Concentrations of 2,4-dinitro-o-sec-butylphenol range from 1.1 to 96.9 micromoles per liter.

Figure 5. MOLECULAR STRUCTURES OF RELATED DINITROPHENOLS

DNP is 2,4-dinitrophenol; DNC is 2,4-dinitro-o-cresol; DNOSBP is 2,4-dinitro-o-sec-butylphenol; DNOCHP is 2,4-dinitro-o-cyclohexylphenol; DNT is 2,4-dinitrothymol, and; DNPCHP is 2,6-dinitro-p-cyclohexylphenol.

Figure 6. ADSORPTION ISOTHERM FOR 2,4,5-T

Capacity for adsorption of 2,4,5-trichlorophenoxyacetic acid on 273-micron Columbia LC carbon at 25°C is plotted as a function of residual concentration, C_{eq}, at equilibrium. The left ordinate gives capacity in units of micromoles of solute per gram of carbon and the right ordinate in units of milligrams of solute per gram of carbon. The points represent experimental data; the line drawn through the data is the calculated Langmuir isotherm.

Figure 7. ADSORPTION ISOTHERM FOR PARATHION

Capacity for adsorption of 0,0-diethyl-0-p-nitrophenyl phosphorothioate on 273-micron Columbia LC carbon at 25°C is plotted as a function of residual concentration, C_{eq}, at equilibrium. The left ordinate gives capacity in units of micromoles of solute per gram of carbon and the right ordinate in units of milligrams of solute per gram of carbon. The points represent experimental data; the line drawn through the data is the calculated Langmuir isotherm.

Figure 8. LANGMUIR PLOT FOR 2,4,5-T

In accord with the Langmuir model for adsorption equilibrium, a linear trace obtains for the isotherm for 2,4,5-trichlorophenoxyacetic acid when $(X/m)^{-1}$ is plotted versus (C_{eq}). The intercept of this plot is $(X_m)^{-1}$ and the slope is $(bX_m)^{-1}$.

Figure 9. LANGMUIR PLOT FOR PARATHION

Equilibrium adsorption for 0,0-diethyl-0-*p*-nitrophenyl phosphorothioate, as for all other pesticides tested, is described well by the Langmuir model for adsorption.

Figure 10. TEMPERATURE DEPENDENCE OF RATE OF ADSORPTION

Rate constants for 0,0-diethyl-0-*p*-nitrophenyl phosphorothioate, 2,4-dichlorophenoxyacetic acid, 2,4-dinitro-*o*-*sec*-butylphenol, and the neutral and anionic species of 4-nitrophenol are plotted on a logarithmic scale versus the reciprocal of Kelvin temperature.

Figure 11. TEMPERATURE DEPENDENCE OF CAPACITY FOR ADSORPTION

Equilibrium capacities for adsorption of 2,4-dinitro-*o*-*sec*-butylphenol and 2,4-dichlorophenoxyacetic acid are plotted on a logarithmic scale versus the reciprocal of Kelvin temperature.

Figure 12. ISOTHERM FOR DNOSBP

Equilibrium capacity for adsorption of 2,4-dinitro-*o*-*sec*-butylphenol is represented in terms of micromoles per gram of carbon on the left ordinate and in terms of milligrams per gram on the right ordinate. A calculated Langmuir isotherm is drawn through the experimental data.

Figure 13. ISOTHERM FOR DNOCHP

The curve drawn through the experimental data for equilibrium adsorption of 2,4-dinitro-o-cyclohexylphenol is a calculated Langmuir isotherm.

TABLE I

SELECTED ORGANIC PESTICIDES AND SOME MOLECULARLY RELATED NITROPHENOLS

Compound	Common Name or Abbreviation	Primary Application as a Pesticide	Molecular Weight	Approx. Solubility of Neutral Molecule in Water at 25°C,* mg/1
2,4-dichlorophenoxyacetic acid	2,4-D	herbicide	221.0	900
2,4,5-trichlorophenoxyacetic acid	2,4,5-T	herbicide	255.5	280
2-(2,4,5-trichlorophenoxy)propionic acid	SILVEX	herbicide	269.5	180
2,4-dinitro-*o*-*sec*-butylphenol	DNOSBP	herbicide, insecticide	240.2	52
2,4-dinitro-*o*-cyclohexylphenol	DNOCHP	acaricide, insecticide	266.2	10
1-naphthyl N-methylcarbamate	SEVIN	insecticide	201.2	99
0,0-diethyl-0-*p*-nitrophenyl phosphorothioate	PARATHION	acaricide, insecticide	291.3	24
4-nitrophenol	PNP	related nitrophenol	139.1	16,000
2,4-dinitrophenol	DNP	related nitrophenol	184.1	6,000
2,4-dinitro-*o*-cresol	DNC	related nitrophenol	198.1	v.sl.s.
2,4-dinitrothymol	DNT	related nitrophenol	240.2	v.sl.s.
2,6-dinitro-*p*-cyclohexylphenol	DNPCHP	related nitrophenol	266.2	v.sl.s.

*All of these compounds with the exception of SEVIN and PARATHION form very soluble salts.

TABLE II

ANALYTICAL DATA FOR ORGANIC PESTICIDES AND MOLECULARLY RELATED NITROPHENOLS

Compound	Wavelength of Maximum Absorption, λ, mμ	Molar Absorptivity 1/mol-cm
2,4-dichlorophenoxyacetic acid	284	1,900
2,4,5-trichlorophenoxyacetic acid	289	2,500
2-(2,4,5-trichlorophenoxy)propionic acid	289	2,500
2,4-dinitro-o-sec-butylphenol	375	14,520
2,4-dinitro-o-cyclohexylphenol	376	14,000
1-naphthyl N-methylcarbamate	279	5,900
4-nitrophenol	anion 400	17,980
(also for PARATHION)	neutral 315	10,000
2,4-dinitrophenol	360	14,820
2,4-dinitro-o-cresol	373	14,040
2,4-dinitrothymol	394	15,240
2,6-dinitro-p-cyclohexylphenol	447	7,075

TABLE III

ADSORPTION CONSTANTS FOR ORGANIC PESTICIDES AND MOLECULARLY RELATED NITROPHENOLS

Compound	Relative Rate Constant,* k, $[(\mu mol/g)^2/hr] \times 10^{-4}$	LANGMUIR EQUILIBRIUM CONSTANTS**	
		X_m, $(\mu mol/g) x 10^{-3}$	b, $(1/\mu mol)$
2,4-dichlorophenoxyacetic acid	1.44	1.75	0.095
2,4,5-trichlorophenoxyacetic acid	1.00	1.75	0.150
2-(2,4,5-trichlorophenoxy)proprionic acid	0.71	1.72	0.145
2,4-dinitro-*o*-*sec*-butylphenol	1.35	1.85	0.174
2,4-dinitro-*o*-cyclohexylphenol	1.12	1.88	0.148
1-naphthyl N-methylcarbamate	1.64	--	--
0,0-diethyl-0-*p*-nitrophenyl phosphorothioate	1.49	1.82	1.22
4-nitrophenol	anion 0.52	--	--
	neutral 1.21	--	--
2,4-dinitrophenol	0.87	--	--
2,4-dinitro-*o*-cresol	1.12	--	--
2,4-dinitrothymol	0.67	--	--
2,6-dinitro-*p*-cyclohexylphenol	0.90	--	--

*Experimental Conditions: $C_o = 10 \mu mol/l$, 25.0 mg/l 0.273-mm Columbia Carbon, 28°C.

**Experimental Conditions: 0.273-mm Columbia Carbon, 25°C.

TABLE IV

THERMODYNAMIC CONSTANTS FOR ADSORPTION

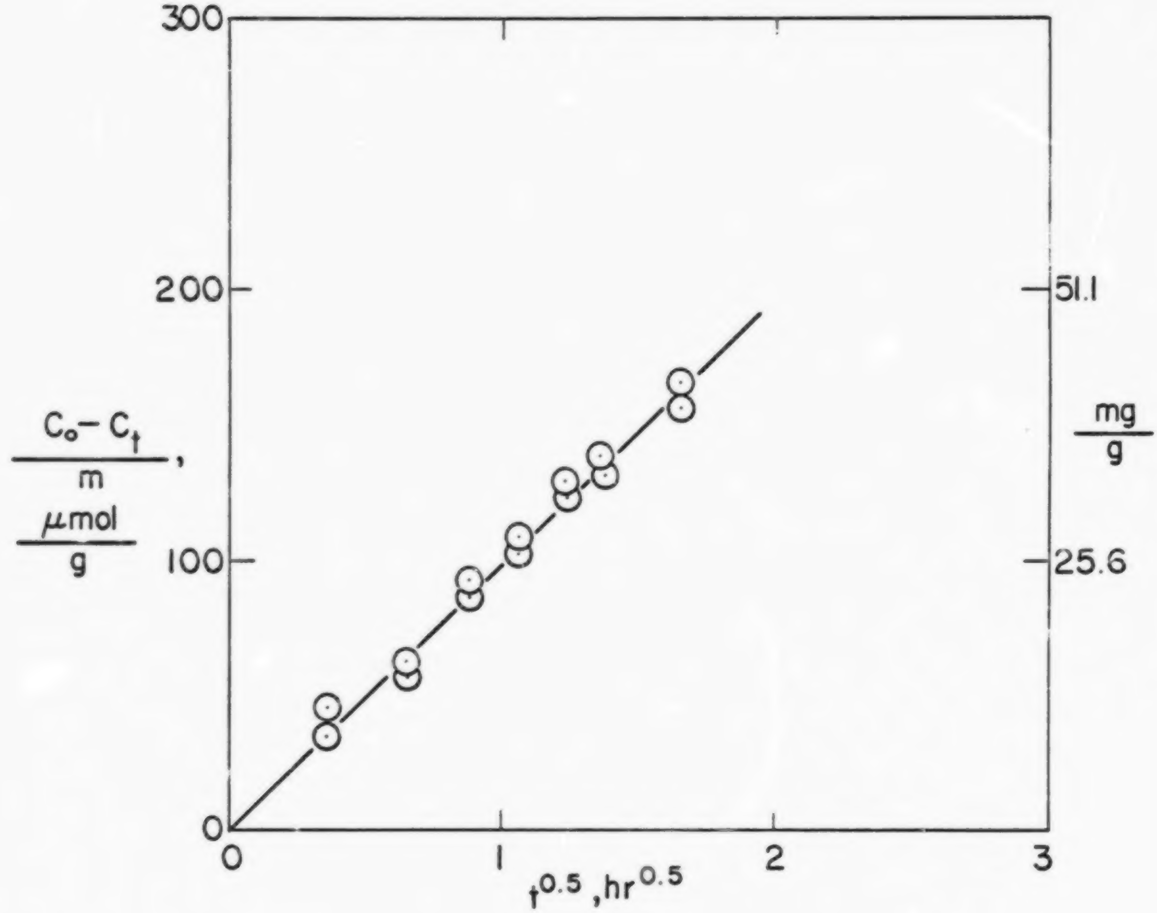
Compound	Activation Energy, E* cal/gmol	Heat of Adsorption, ΔH cal/gmol
2,4-D	2,740	-4,160
DNOSBP	2,380	-4,190
PARATHION	9,650	--
PNP (neutral)	8,890	--
PNP (anion)	2,260	--

*Based on relative rate constant, k.

TABLE V

COMPARISON OF LANGMUIR EQUILIBRIUM CONSTANTS FOR ORGANIC PESTICIDES AND SELECTED ADSORBATES

Compound	X_m		b^{-1}	
	mmol/g	mg/g	µmol/l	mg/l
2,4-D	1.75	387	10.5	2.32
2,4,5-T	1.75	448	6.7	1.71
SILVEX	1.72	464	6.9	1.86
DNOSBP	1.85	444	5.8	1.39
DNOCHP	1.88	500	6.8	1.81
PARATHION	1.82	530	0.82	0.24
PHENOL	1.09	103	9.3	0.87
SULFONATED 2-DODECYLBENZENE	0.40	139	0.22	0.078
1-CHLORO-4-NITROBENZENE	2.52	400	1.4	0.22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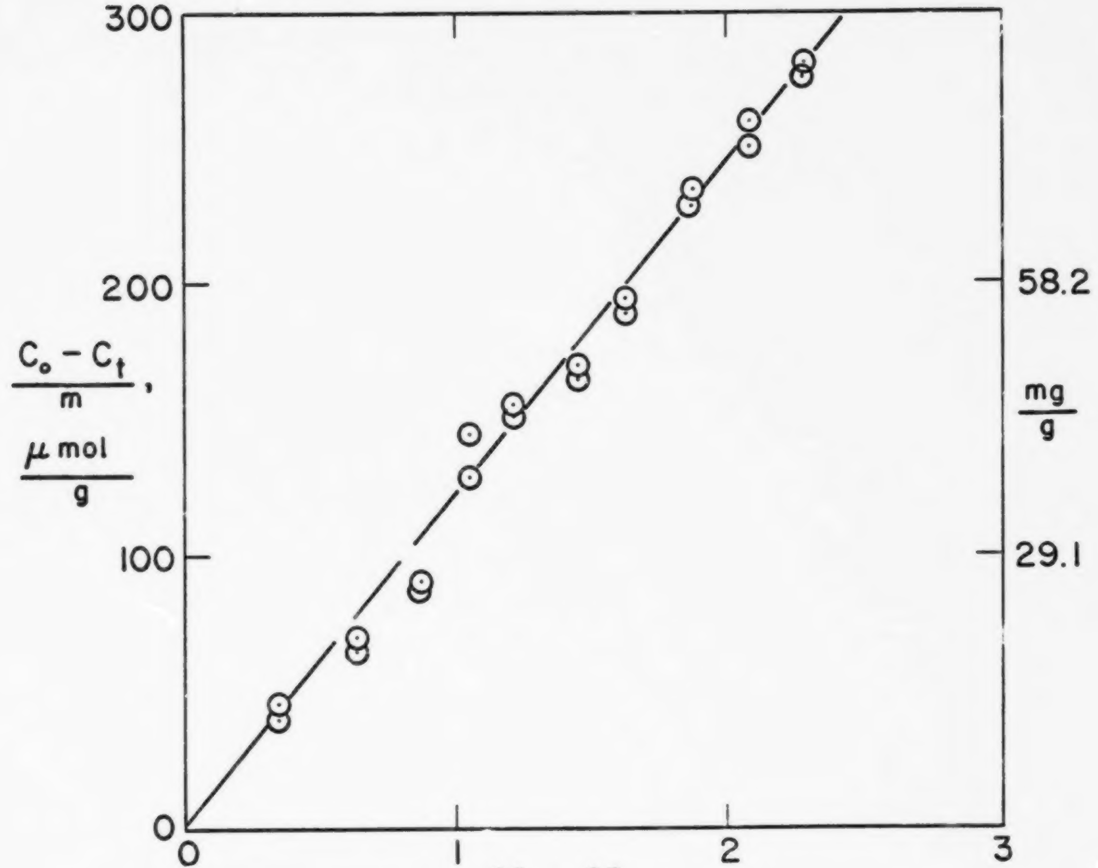
200
100
0
0
1
2
3
$\frac{C_o - C_t}{m}$,
$\frac{\mu mol}{g}$
51.1
25.6
$\frac{mg}{g}$
$t^{0.5}$, $hr^{0.5}$

Figure 1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29.1
$\frac{mg}{g}$
0
1
2
3
$t^{0.5}$, $hr^{0.5}$

Figure 2

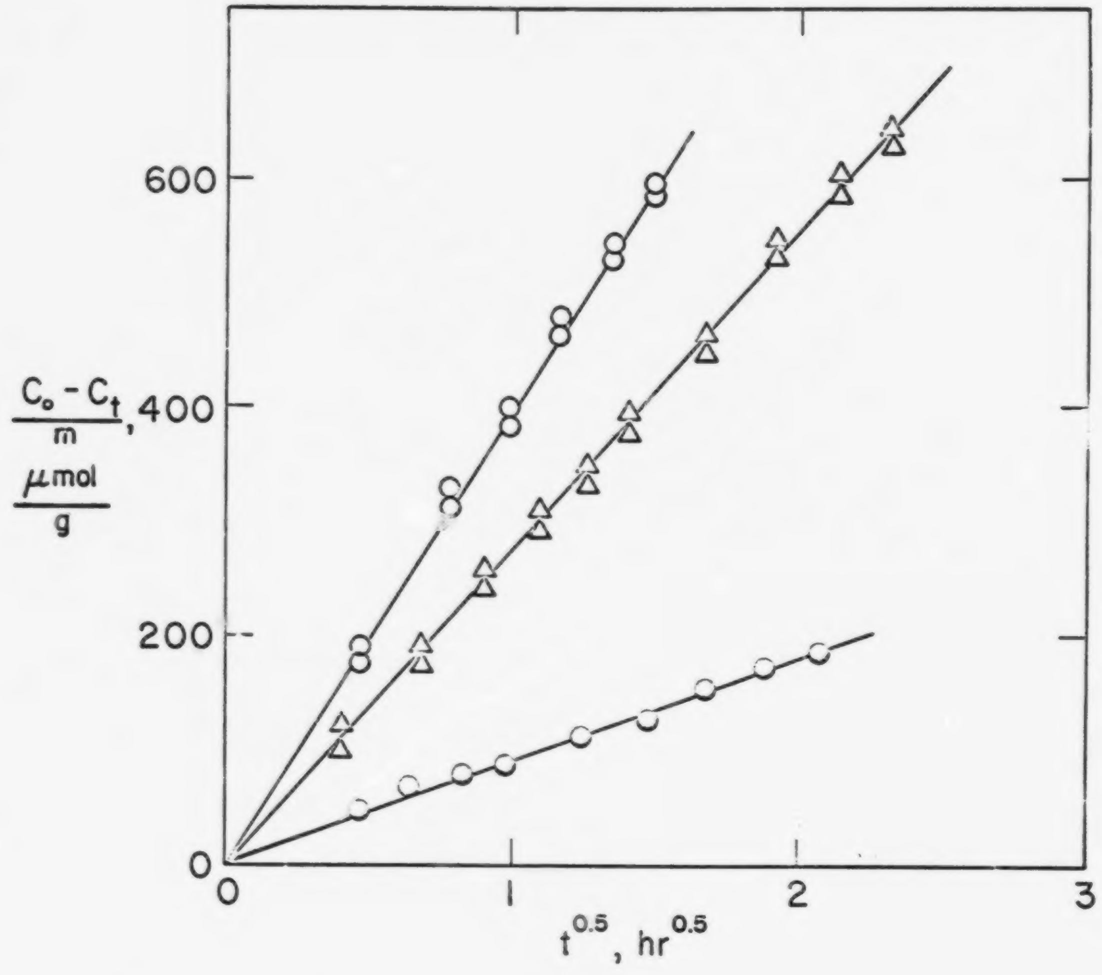


Figure 3

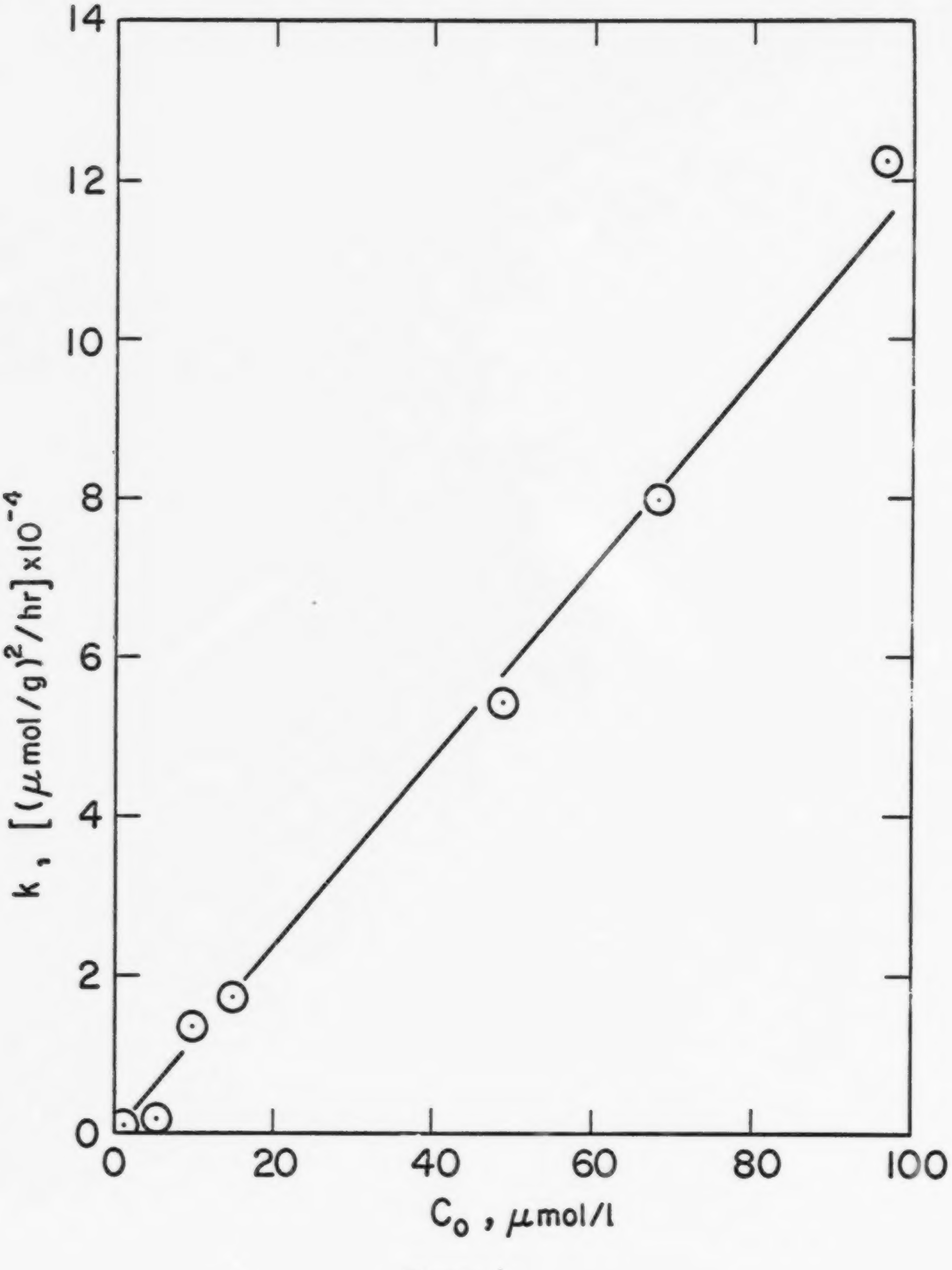
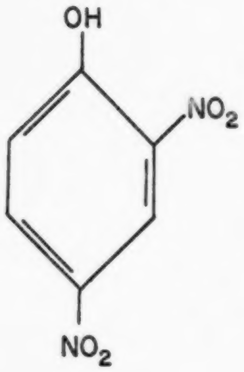
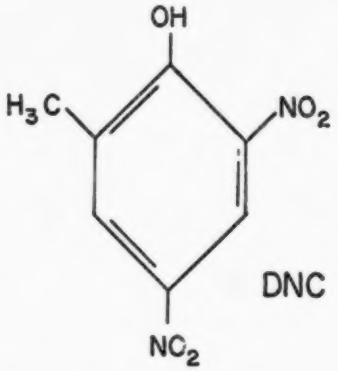


Figure 4



DNP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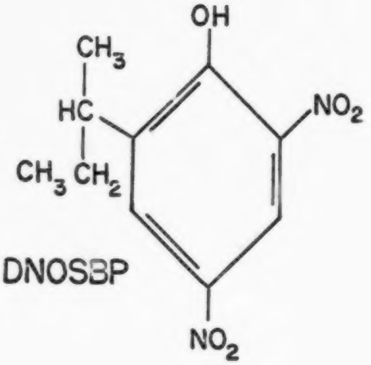
H3C
NO2
NO2

DNC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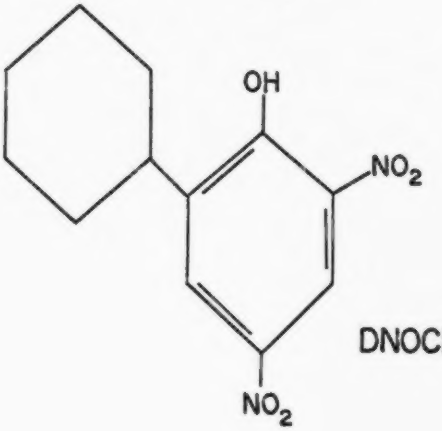
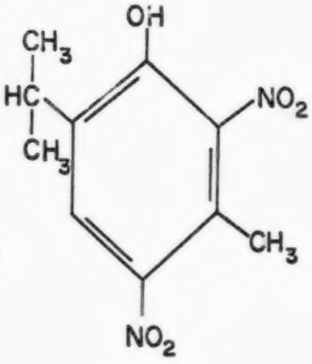
HC
CH3 CH2
NO2
NO2

DNOSBP



DNOCHP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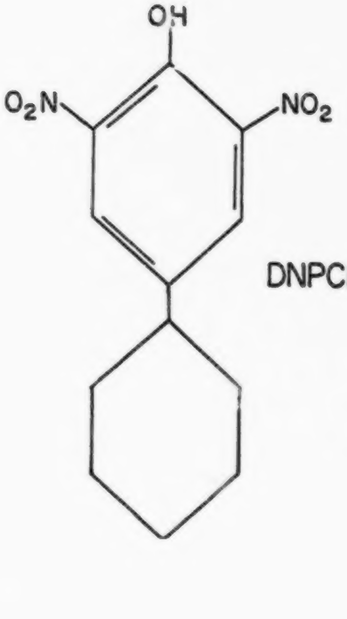
HC
CH3
NO2
CH3
NO2

DNT



DNPCHP

Figure 5

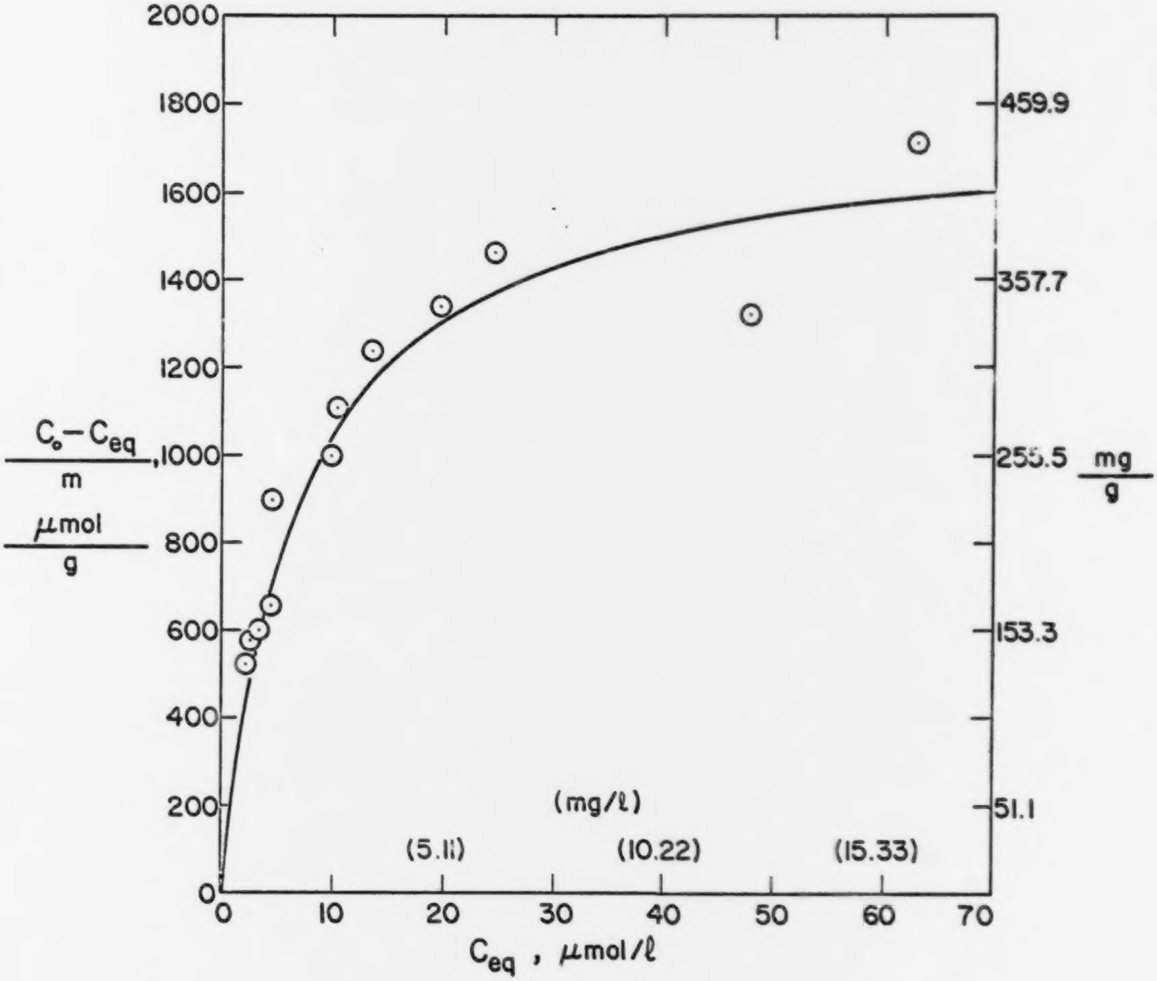
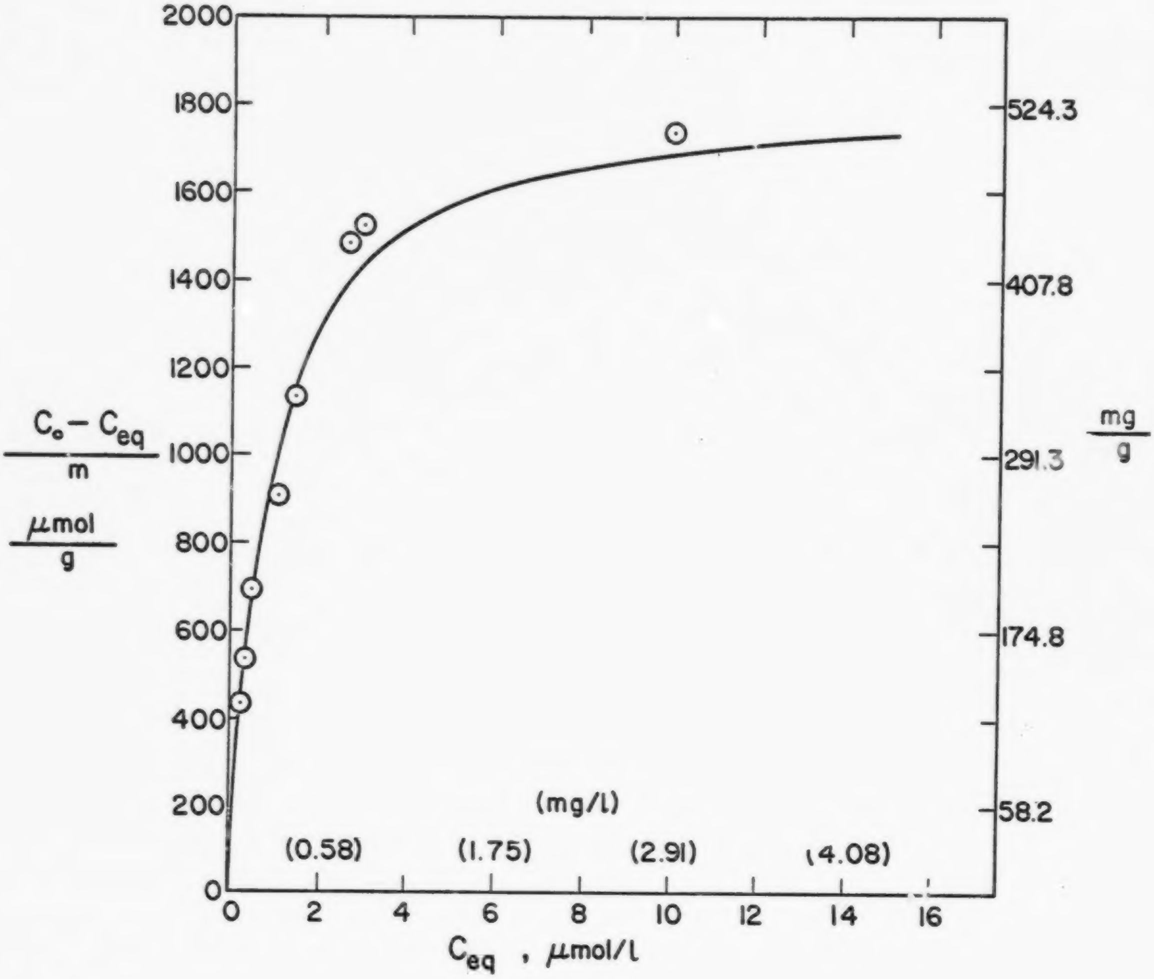

2000
1800
1600
1400
1200
1000
800
600
400
200
0
$\frac{C_o - C_{eq}}{m}$,
$\frac{\mu mol}{g}$
459.9
357.7
255.5
153.3
51.1
$\frac{mg}{g}$
(mg/ℓ)
(5.11)
(10.22)
(15.33)
0
10
20
30
40
50
60
70
C_{eq} , μmol/ℓ

Figure 6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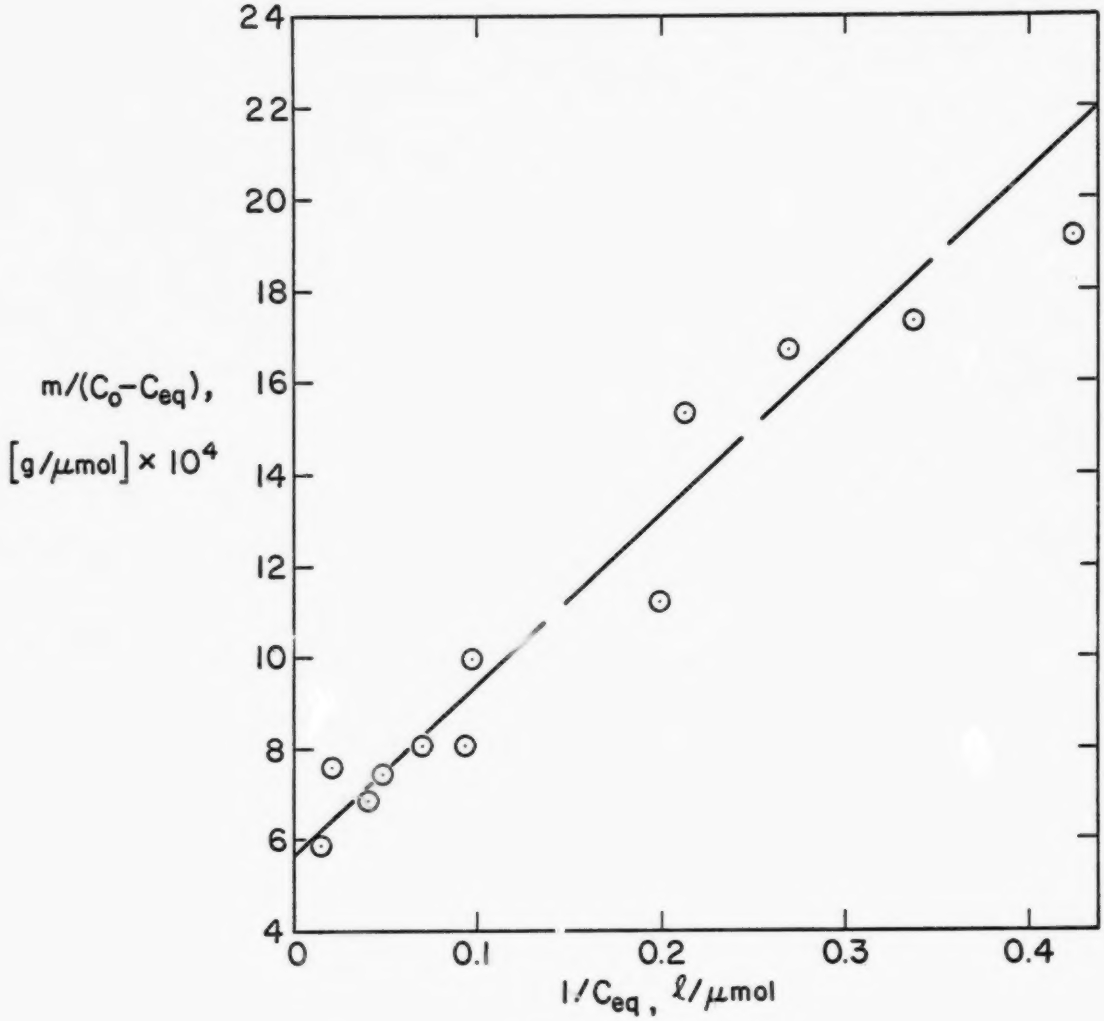
1800
1600
1400
1200
1000
800
600
400
200
0
$\frac{C_o - C_{eq}}{m}$
$\frac{\mu mol}{g}$
524.3
407.8
291.3
174.8
58.2
$\frac{mg}{g}$
(mg/l)
(0.58)
(1.75)
(2.91)
(4.08)
0
2
4
6
8
10
12
14
16
C_{eq}, μmol/l

Figure 7


24
22
20
18
16
14
12
10
8
6
4
m/(C_o–C_{eq}),
[g/μmol] × 10^4
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0.1
0.2
0.3
0.4
1/C_{eq}, ℓ/μmol

Figure 8

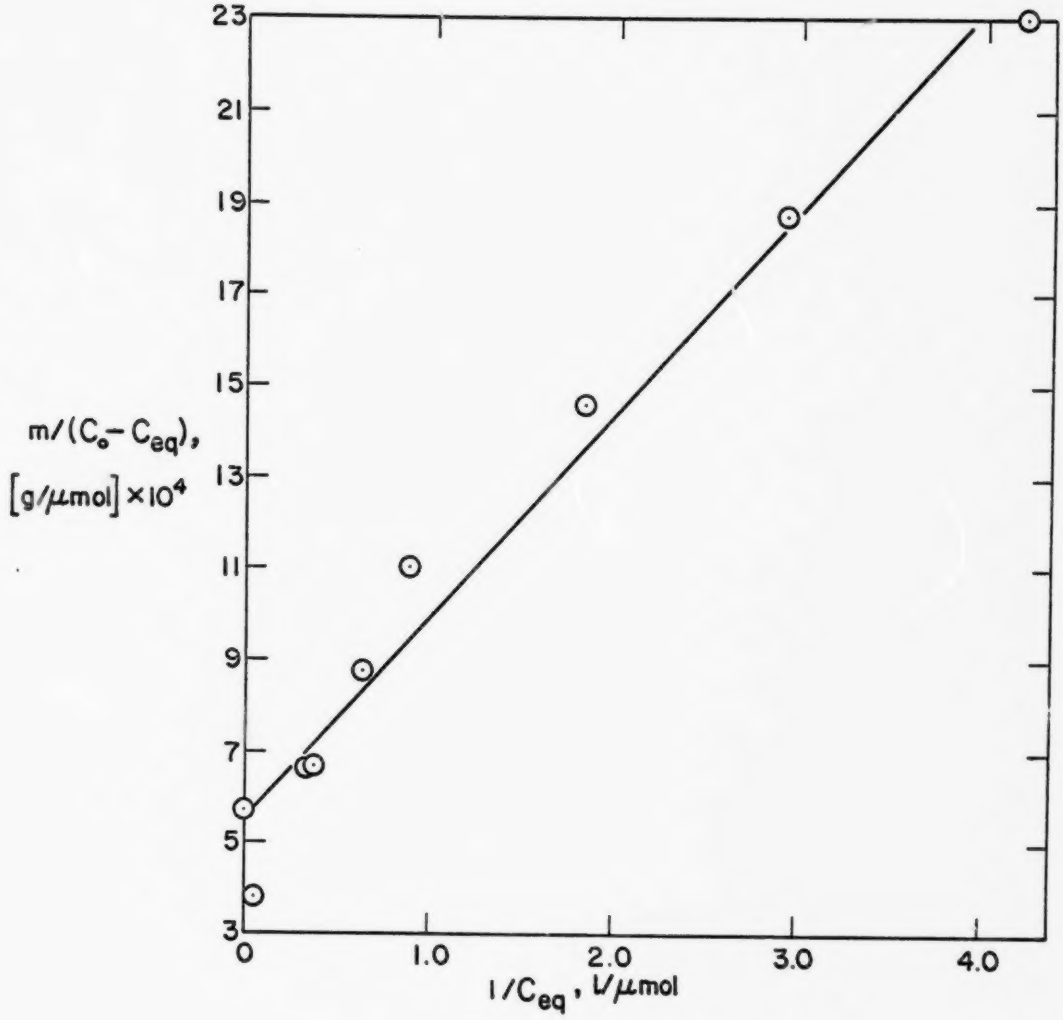

$m/(C_o - C_{eq})$,
$[g/\mu mol] \times 10^4$
23
21
19
17
15
13
11
9
7
5
3
0
1.0
2.0
3.0
4.0
$1/C_{eq}$, $l/\mu mol$

Figure 9

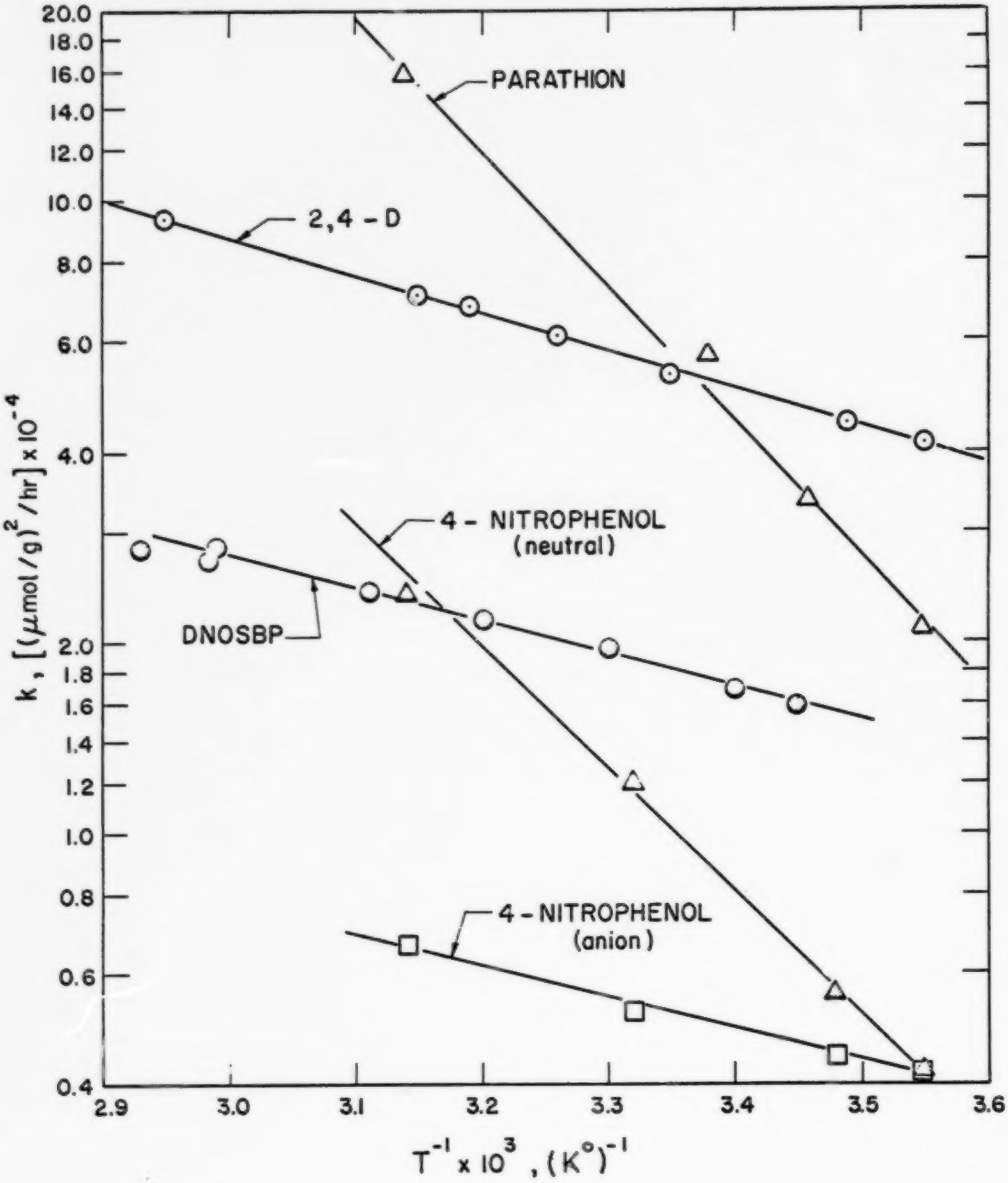

PARATHION
2,4 - D
4 - NITROPHENOL (neutral)
DNOSBP
4 - NITROPHENOL (anion)
k, $[(\mu mol/g)^2/hr] \times 10^{-4}$
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
2.9
3.0
3.1
3.2
3.3
3.4
3.5
3.6
$T^{-1} \times 10^3$, $(K^\circ)^{-1}$

Figure 10

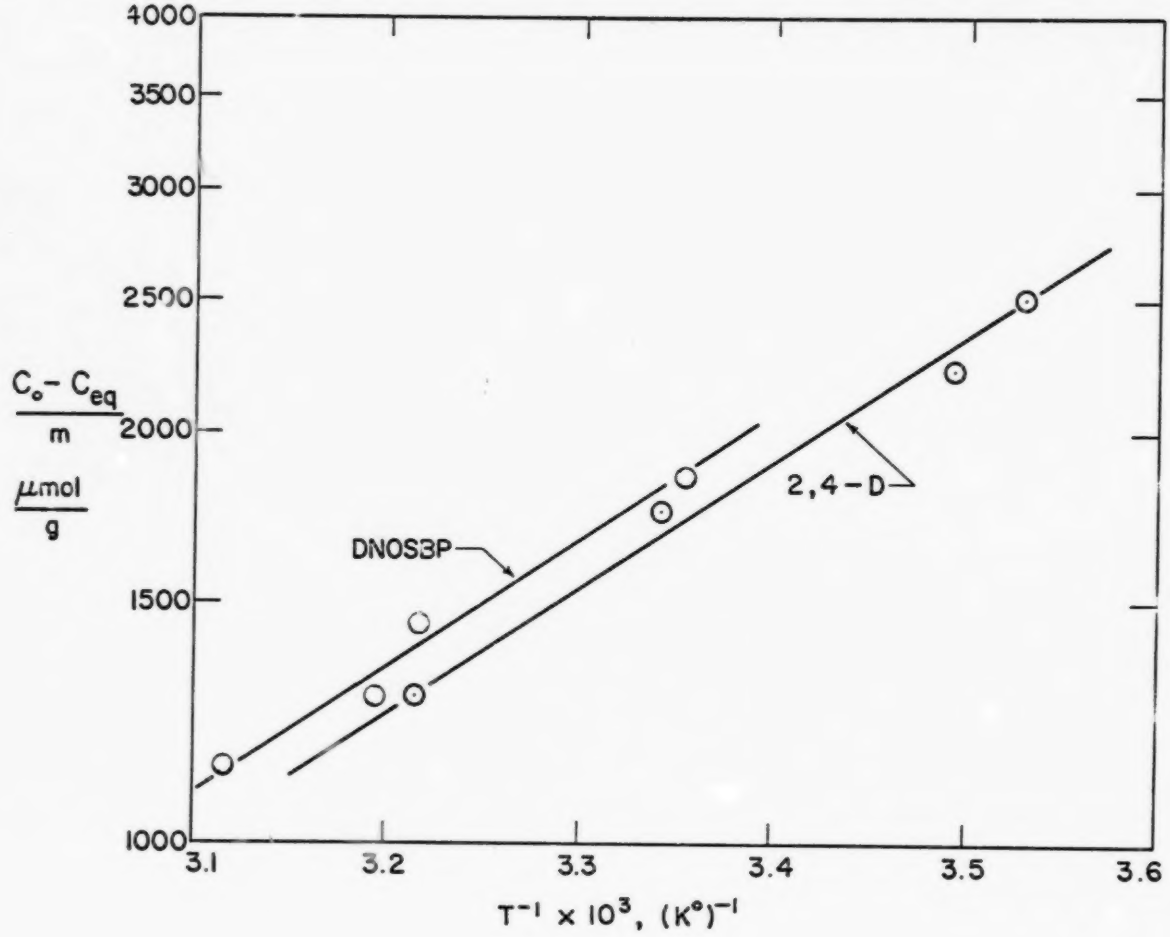
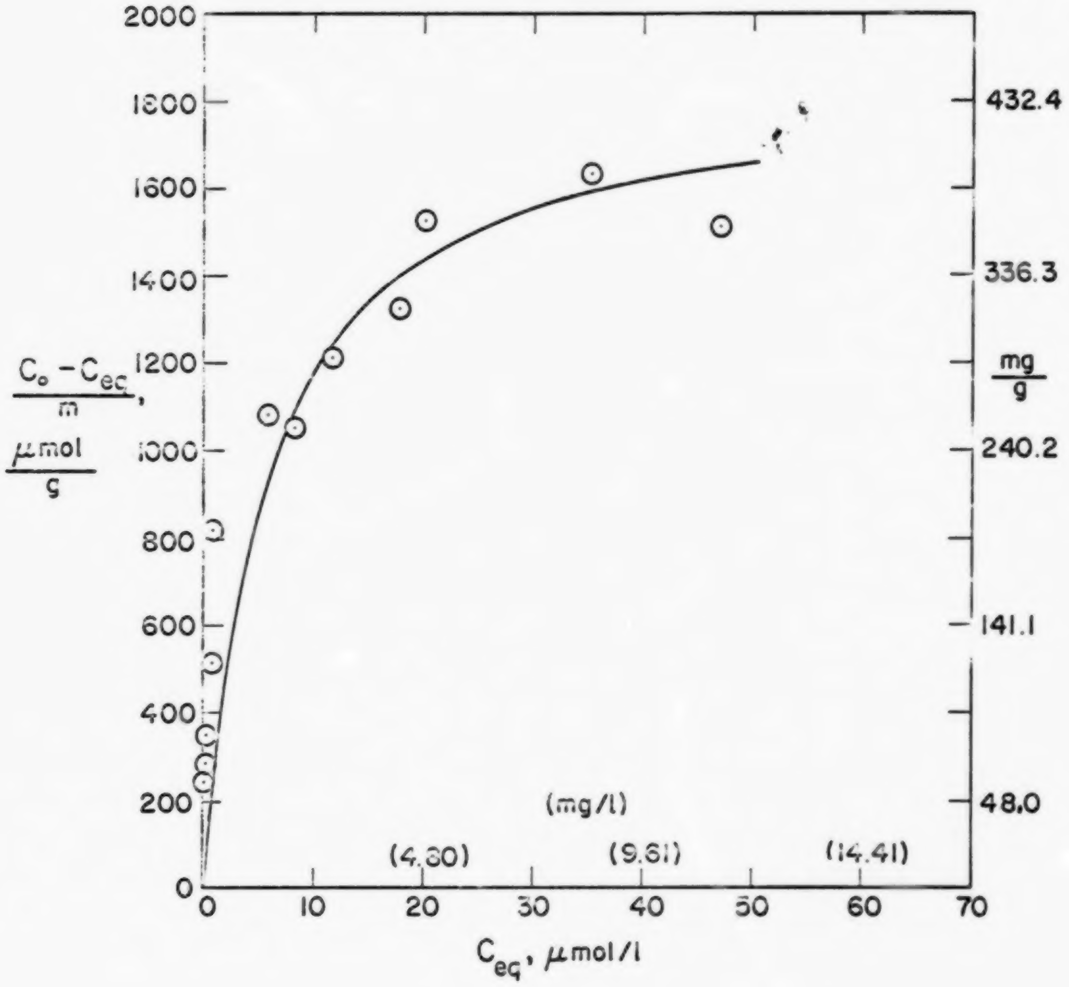

4000
3500
3000
2500
2000
1500
1000
$\frac{C_o - C_{eq}}{m}$
$\frac{\mu mol}{g}$
3.1
3.2
3.3
3.4
3.5
3.6
$T^{-1} \times 10^3$, $(K°)^{-1}$
DNOSBP
2,4-D

Figure 11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1800
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1200
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600
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$\frac{C_o - C_{eq}}{m}$,
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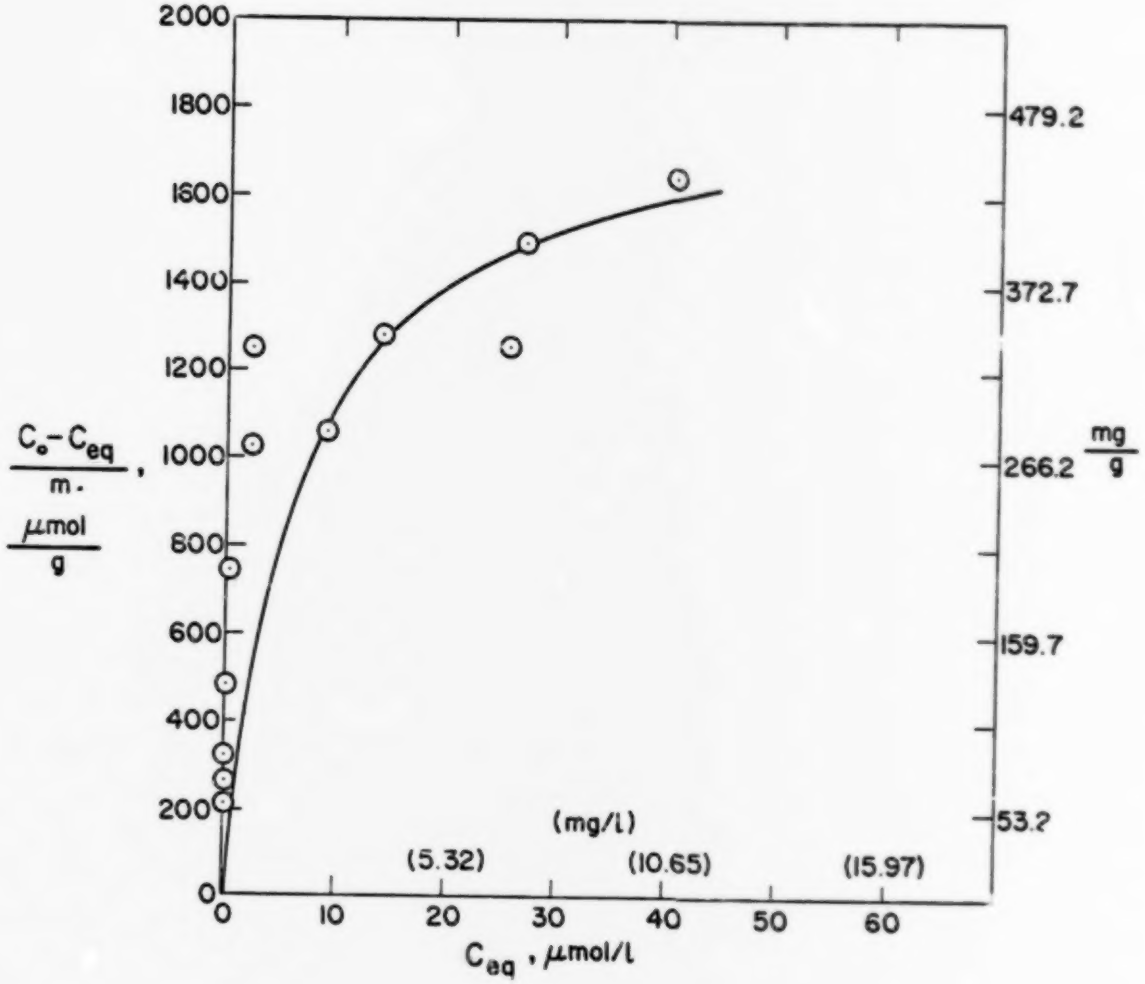
336.3
240.2
141.1
48.0
$\frac{mg}{g}$
(mg/l)
(4.80)
(9.61)
(14.41)
0
10
20
30
40
50
60
70
C_{eq}, μmol/l

Figure 12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1200
1000
800
600
400
200
0
$\frac{C_o - C_{eq}}{m}$, $\frac{\mu mol}{g}$
479.2
372.7
266.2
159.7
53.2
$\frac{mg}{g}$
(mg/l)
(5.32)
(10.65)
(15.97)
0
10
20
30
40
50
60
C_{eq}, µmol/l

Figure 13

THE STRUCTURE AND SURFACE CHEMISTRY OF ACTIVE CARBON

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Exacting demands are being made upon existing water resources to meet the requirements of a highly industrialized society. These demands can be expected to mount in the future, for continuing population expansion and technological development lead naturally to both more extensive and more intensive use of available supplies of water, and ultimately to the pollution and degradation of the quality of these waters. Much of the water currently available to a large segment of society has been subjected to previous use. Indeed, multiple reuse of water is not uncommon today; planned and deliberate reuse is expected to be an even more significant factor in water resources management in the years ahead. It is evident that as reuse practice increases, more stringent requirements will be placed on the treatment of waters and wastewaters, and more effective removal of materials which might otherwise persist and build up to intolerable concentrations during several reuse cycles will be required.

Adsorption on active carbon has within the past several years emerged as a particularly attractive method for removal of perdurable organic pollutants from waters and wastewaters. Although active carbon has been rather widely employed for the past three or four decades for removal of taste-and odor-producing materials from water supplies, its use in this application has been largely occasional and for the most part quite inefficient. While it has been possible to tolerate such inefficiencies in an application involving relatively low concentrations of pollutants, extensive treatment of wastewater for direct reuse will require that this process be developed to a high degree of effectiveness and efficiency for obvious technological and economic reasons.

In order that engineers responsible for the design of active-carbon facilities for water or waste treatment be in position to articulate specifications for maximum efficiency of use in particular situations, they must have at their disposal precise information about the nature and behavior of active carbon and about the adsorption process. Much recent research has centered on the development of such information for this purpose(1,2,3,4,5), but there is yet more to be learned and set forth regarding the properties and surface chemistry of active carbon and about factors which affect its behavior as an adsorbent. Active carbon is effective for removal of organic substances of relatively low solubility in water primarily because it provides a large interfacial area at which such substances may accumulate. However, any interpretation of the adsorptive behavior of active carbon based solely on the extensiveness of the surface of this material is obviously incomplete, for it is well known that equal weights of two carbons prepared from different raw materials and/or by different methods may possess the same total surface area yet function differently as adsorbents. Part of such differences in adsorptive behavior can be explained in terms of relative pore size distributions, but part must also be attributed to differences between the respective surface properties of the carbons. It must be recognized that the surface of any active carbon is comprised in part of residual electron- and ion-exchange functional groups, connected by electron-conducting bond systems.(6) The nature of these functional groups is determined to a large extent by the method of activation as well as by the type of raw material from which the carbon is prepared. With the existence of electron- and ion-exchange groups at the surface of carbon, it is reasonable to expect that electrolytes in solution may interact with the carbon to influence its behavior as an adsorbent. Indeed, it is conceivable that such interactions could markedly affect the overall adsorption process under certain conditions, possibly effecting changes in the process which may be put to good advantage to achieve higher efficiency or enhanced effectiveness of removal of pollutants. Weber and Morris(4), for example, have shown that the hydrogen-ion activity of a solution affects both rate and capacity for adsorption of negatively charged species of sulfonated alkylbenzene from aqueous solution by carbon. These authors have interpreted their results as indicating that with decreasing pH there is an increasing association of the positively-charged hydrated proton with negatively-charged functional groups on the active carbon surface, thus neutralizing electrostatic repulsive forces to allow the charged organic species to more easily migrate through the pore spaces and be adsorbed at inner surface sites. Garten and Weiss(6) have interpreted changes in hydrogen-ion activity observed upon addition of active carbon to acidic or basic solutions in terms of an interaction between the acid or base and a basic or acidic heterocyclic surface structure, respectively. This interaction is currently being studied in detail in the authors' laboratories to determine more precisely its effect on the sorptive properties of active carbon.

Other inorganic species also seem to be important in their effects on the manner in which active carbon functions in aqueous solution as a sorbent for organic substances. Joyce and Sukenik(1) have observed a 50% increase in ash content (from 6 to 9% and from 12 to 18%) to be accompanied by a 50% decrease in the capacity of an active carbon after ten cycles of sorption from a solution of the calcium salt of a sulfonated alkylbenzene followed by thermal regeneration. Because the ash was found to be soluble in acid solution, but insoluble in near neutral solution, these authors suggest that acid treatment in conjunction with thermal regeneration may prove feasible as a means for restoring active carbon to near original capacity. Before such treatment is effected however, it should be known how the acid may affect the active carbon surface, and, therefore, how it may influence the adsorption process.

Various chemical oxidizing agents can also interact with active carbon in aqueous solution to increase the amount of chemisorbed oxygen at the carbon surface.(7) Once more, however, the effect of the presence of this oxygen on the sorptive properties of active carbon has not yet been well enough defined.

It is apparent then that much more information is needed regarding the nature of interactions which occur between the various functional surface groups of active carbon and electrolytes in aqueous solution, with particular reference to the effects of such interactions on the sorptive properties of the carbon. The present discussion has as its objective the examination of such information as is currently available concerning the structure and nature of active carbon, and the presentation of a relatively unified concept or model for description of the surface chemistry of this material. This model will hopefully provide a reasonable basis for further research directed to the delineation of the surface properties of carbon significant in its applications for water and wastewater treatment.

Preparation of Active Carbon

The term active carbon actually implies a rather broad family of substances, with individual species being characterized by sorptive and catalytic properties rather than by definite structure or specific chemical composition.(8) Particular properties may be imparted to an active carbon either by starting with different raw materials or by utilizing different preparative procedures.

Substances from which active carbons are manufactured are carbonaceous in nature, usually carbohydrates; wood, coal, sugar, nut shells, and vegetable matter are examples of typical raw materials. It should be noted that many of the differences commonly ascribed to dissimilar starting materials may be due in fact to non-carbonaceous impurities in the raw materials. In addition to differences which obtain as a result of the particular characteristics of the starting material, preparative conditions may be varied and selected additives employed to produce a particular active carbon of desired structure and surface properties.

The production of active carbon involves first the formation of a char from the raw material. The starting material is heated - usually in the absence of air - to a temperature sufficient to effect drying and to drive off volatile fractions. Carbonization is then accomplished by elevating the temperature, producing a carbonaceous char.(2,8) In this process the temperature is increased slowly to allow time for each step to be completed before the next begins.(2) The entire process is usually carried out below 600°C, although exceptions do exist. Additives such as calcium chloride, magnesium chloride, zinc chloride, or any one of a number of similar materials may be used to catalyze the process and to impart certain characteristic properties to the finished product.(8)

The char developed in the carbonization process has relatively little internal surface area, and because a large surface is required for most adsorption applications, the char is generally "activated" by treatment with oxidizing gases under carefully controlled conditions. The oxidizing gases - commonly carbon dioxide, steam, and air(6) - attack the more readily oxidizable portions of the char, resulting in the development of a porous structure and an extensive internal surface. The temperature of activation is a critical factor in the process, as will be discussed in more detail shortly. Treatment of the char with reagents such as chlorine, dolomite sulfates and several other substances to develop special properties in the finished product and to catalyze the action of the oxidizing gas is often effected prior to the activation process.(8) According to Johnson, et al.(2), carbonization and activation can sometimes be carried out in one step, rather than as separate operations. The total surface area of a carbon, by far the greatest percentage of which is internal, can be as great as 2,500 square meters per gram after activation.

Structure and Structural Development

The molecular and crystalline structure of active carbon is an important determinant of the types of functional groups which can exist on the surface, and is therefore an important consideration in any discussion of the surface chemistry of this material. Although there is little direct information available on the structure of active carbon, much can be derived from existing data on the structure of carbon black. Very little chemical difference exists between these two substances and the only apparent physical difference is that the carbon black has much less internal surface area.(6)

As a basis for discussion of the active carbon structure, it is appropriate to consider first the structure of ideal graphite in that it is closely approximated in the basic structural unit of both active carbon and carbon black.(10,11,12)

The structure of ideal graphite is given in Figure 1. According to Walker(12), this structure is composed of a system of infinite layers of fused hexagons. Within each layer the carbon-carbon bond distance is 1.415 Å indicating one-third double bond character. Three of the carbon's four electrons are engaged in forming regular covalent bonds with neighboring atoms and are localized, while the fourth resonates between several valence-bond structures, giving each carbon-carbon bond a one-third double bond character. Relatively weak van der Waals forces act between the parallel layers to hold the distance of separation to approximately 3.35 Å. The carbon layers form an a-b-a-b-a-b stacking sequence in which one-half of the carbon atoms in any one plane lie above the center of the hexagons in the layer immediately below it. The carbon atoms are directly superimposed in alternate layers. X-ray diffraction spectra obtained for most natural graphites indicate that this structural configuration is in fact predominant.(12)

During the carbonization of the raw material in the preparation of active carbon, small aromatic nuclei, interpreted from X-ray spectrographs as microcrystallites consisting of fused hexagonal rings of carbon atoms having a structure similar to that of graphite, are formed.(10,11) The diameter of the planes making up the microcrystallite has been estimated as 20-50 Å.(10) The height of stacking is also in the range of 20-50 Å, indicating that each microcrystallite consists of 5-15 layers of aromatic planes.

Although the structure of the microcrystallite is similar to that of graphite, it differs in many ways. During the formation of the microcrystallite, impurities should be expelled from its interior. However, Walker(12) states that interior vacancies exist in the microcrystallite and that their formation depends on the method of preparation. It is possible that these vacancies contain some of the impurities; perhaps the presence of impurities in fact influences the formation of such a vacancy. In addition, the ringed structures at the edges of the planes making up the microcrystallite are often heterocyclic due to the nature of either the starting material or of the preparation process used.(6) Heterocyclic groups would tend to affect both the distance of separation of adjacent planes and the sorptive properties of the carbon. Also, orientation between adjacent planes in the microcrystallite varies from that found in ideal graphitic structure to that of complete random orientation found in turbostratic carbons.(12) The definite a-b-a-b-a-b stacking order, therefore, does not exist in most active carbons. Functional groups terminating the microcrystallite planes interconnect the microcrystallites, and are at least partially responsible for the turbostratic character in that they prevent orientation of the planes with respect to each other. Because of its special properties and the many differences between it and graphite, Garten and Weiss(6) have chosen to compare active carbon to a complex organic polymer rather than to a graphitic type particle.

The structure of the char particle is developed further by treatment with oxidizing gases at high temperature during the activation process. Dubinin, et al.(14), have noticed two stages of oxidation in the activation of carbonized sucrose. First, macropores were formed by the burnout of the most reactive material, consisting principally of hydrocarbon radicals attached to the edge carbons of the microcrystallite. Second, micropores were formed mainly by the burnout of microcrystallite planes. The diameter of the micropore is generally on the order of 4-10 Å, while the macropore diameter is usually much larger.(9) The majority of internal surface area is contributed by the walls of the micropore. Snow, et al.(15), have found that higher ash content causes faster pore development during activation. Inorganic matter appears to cause stress localizations on the surface of the microcrystallite at which points oxidation is initiated much more easily. Once a plane is attacked by an oxidizing gas, oxidation of that plane continues in preference to another area until a stable structure is developed.(10)

Carbonization and activation temperatures are significant considerations in the structural development of active carbons. Riley(16) has demonstrated that the size of the microcrystallites of carbons prepared from carbohydrates increases with increasing temperature of carbonization. In addition, the mechanical strength and electrical conductivity of a carbon increase when prepared at temperatures above 700°C. The temperature at which activation is effected is important also because carbonization continues during this process via the mechanisms of actual removal, cracking, or cyclization of functional groups present at the edges of the microcrystallite.(10)

Chemical Nature of the Active Carbon Surface

Proceeding on the basis of the structure outlined above, and neglecting for the moment the effects of non-carbonaceous impurities, two major types of surfaces can be postulated for active carbon; the planar surfaces of the microcrystallites and the edges of the carbon planes making up the sides of the microcrystallite.

The planar surfaces are probably relatively uniform in nature. No attached functional groups should be present because the electrons of the carbon atoms are involved in covalent bonding with neighboring carbon atoms. Because oxidation occurs much more readily at the edge of the carbon plane than on the surface of the plane(17), few vacancies due to oxidation during the activation process are expected in the surface plane. The majority of the sorptive processes occuring on this surface would be due then to the relatively weak van der Waals bonding forces, although electrons are available for π-bonding if the sorbate is capable of entering into such a bond.(18) Because most of the surface area of a carbon particle is found in the micropores, and because micropores are formed by the "eating out" of microcrystallite planes(10), the larger percentage of the total surface area is probably of the planar-surface type.

The sides of the microcrystallites are more heterogeneous than the planar surfaces, and are characterized by various types of functional groups and vacancies due to the action of oxidizing gases. Corners or raised positions on the surface have the greatest tendency to participate in the electron-sharing reactions which characterize chemisorption.(19) Sorption in depressions is probably physical in nature, but the bonds formed in this case should be much stronger than the bonds formed in physical sorption on the planar surface of the microcrystallite.(19)

Although surfaces of the preceding types can be expected for a very pure active carbon, many carbons have large percentages of oxygen, hydrogen and inorganic ash. The concept of the type of surface available for sorption must be modified somewhat when such substances are present. The presence of hydrogen on the surface of active carbon, for example, lends quite definite properties to that surface. Certain sorption reactions are known to be more or less specific for surfaces comprised of hydrogen sites. Kipling and Shooter(20), have found that iodine vapor adsorption on Spheron 6 can be interpreted in terms of adsorption on that part of the surface covered with hydrogen sites, to the exclusion of those portions of the surface covered with oxygen-containing functional groups. Hydrogen presumably exists either in the form of terminal groups on the fused aromatic planes of the microcrystallite or as part of the hydrocarbon functional groups attached to these planes.(10) Wolff(9) has found that hydrogen is present in amounts ranging from eight to nineteen times that of oxygen, on a molar basis, for carbons containing 0.94 - 2.25% oxygen by weight.

Inorganic matter is present in most commercial active carbons to a very significant extent, and its presence has many noticeable effects.(8,9) The total amount present consists of inorganic constituents originally present in the starting material, and various inorganic salts added to catalyze the carbonization and activation processes or to impart special sorptive properties such as selectivity to the active carbon. The fact that strong acid will remove almost all of the ash content of active carbon suggests that the inorganic matter exists primarily on the microcrystallite surfaces.(9,21) The special properties which the inorganic salts develop possibly are due to their effect on the active carbon surface and to their interactions with the sorbate or other solution constituents. Sorption on a surface covered with tightly-held inorganic species would very likely differ in nature from sorption on an active carbon surface free of such species. Pore structure would also be affected differently by different types of salts used to catalyze the activation process. Possible interactions between the inorganic salts on the active carbon surface and the sorbate or other solution constituents include complex formation, ion-pair formation, precipitation reactions, and oxidation-reduction reactions. Basic studies of the sorptive properties of active carbon should include a careful study of the effect of the active carbon's inorganic constituents.

Electron-spin-resonance studies of active carbon have suggested free-radical structures or structures with unpaired electrons in the microcrystallite.(22) According to Ingram(23), large numbers of unpaired electrons are trapped during the carbonization period due to bond breakage at the edges of the planar structures. These electrons are resonance stabilized. Studies by Harker, et al.(22), have indicated that oxygen interacts with these electrons to form oxygen complexes on the surface. The only means by which this oxygen can be removed is as oxides of carbon by degassing at high temperature.(22)

Oxygen, one of the major non-carbon constituents of active carbon, constitues 2 - 25% by weight of this material, the exact amount present depending upon the temperature and method of activation.(10) The temperature of activation ranges from 400 to 1,200°C, and the oxygen content decreases with increasing temperature of activation.(13) Heating carbon at a temperature of 1,000 - 1,200°C in a high vacuum removes nearly all of the oxygen from the carbon surface, usually as oxides of carbon. For this reason oxygen is thought to exist in structures on the surface of the microcrystallite or between carbon planes near the surface of the microcrystallite.(16)

The presence of oxygen complexes on the surface of the carbon affects the sorptive properties of this material in that they tend to increase the polarity of the surface.(24) In aqueous solution, therefore, a stronger solvent-active carbon bond must be broken before sorption of the sorbate can occur if oxygen complexes exist at the carbon surface. Excluding any specific oxygen complex-sorbate interaction, increased polarity decreases the quantity of non-polar sorbate removed from solution by the carbon. For a polar sorbate, the oxygen complex-sorbate interaction usually is stronger, compensating, at least in part, for the added energy required to desorb water. Kipling(25) has found that oxygen on the surface of carbon affects the specificity of sorption from an organic, binary liquid solution. As indicated previously, Kipling and Shooter(20) have reported that iodine apparently does not adsorb on that portion of the active carbon surface covered with oxygen sites, but does adsorb on the part of the surface covered with hydrogen sites. These authors also indicate that the normally strong lateral interaction of adsorbed idodine molecules appear to be lessened in the presence of the oxygen, thus preventing attainment of the extent of uptake realized in the absence of surface oxygen. An additional consideration is that sorbates which have a natural tendency to combine with oxygen probably sorb more easily on oxygenated surfaces that they do on non-oxygenated surfaces.

Oxygen can be added to an active carbon in one or more of three principal ways. If the starting material contains oxygen, this may become incorporated into the microcrystallite surface structure during the manufacture of the carbon.(16) If the starting material is a carbohydrate, for example, heating will cause condensation and cyclization of the carbohydrate with the inclusion of an oxygen atom in the ringed structure as an ether oxygen. As a second possibility, oxygen can be sorbed on active carbon at room temperature. Part of the oxygen added in this manner can be evacuated at room temperature - this phenomenon being known as "the reversible effect" - while another part requires evacuation at temperatures in excess of 1,000°C.(22) The latter phenomenon, which has been studied by electron spin resonance methods, is known as "the surface oxide effect". Thirdly, oxygen can be chemisorbed on the surface of the active carbon during treatment with oxidizing agents. As previously indicated, the principal oxidizing gases in the activation process are air, steam and carbon dioxide. These three gases form oxygen complexes at the surface of the carbon which can be removed - as carbon monoxide, carbon dioxide and water vapor - only by degassing at very high temperatures.(8,26) Treatment of active carbon with chemical oxidizing agents in aqueous solution also leads to the chemisorption of oxygen on the surface of the carbon.(7,26,27)

Characterization of Oxygen Surface Structures

Because of their numbers and their probable effects on the sorption process, oxygen complexes on the surface of carbon merit careful consideration.

One of the principal methods for study of the nature of oxygen structures on carbon has been by simple acidimetric-alkalimetric titrations, and major interest has focused on the very important variable of temperature of activation. Garten and Weiss(6) have provided an excellent review of the findings of such research, and these may be summarized briefly as follows:

1. Carbon activated at 400°C (L-Carbon) will sorb base but not acid from aqueous solution while carbon activated at 800 - 1,000°C (H-Carbon) will sorb acid but not base.
2. Carbon activated at intermediate temperatures will sorb both acid and base.
3. Capacities for both acid and base are usually in the milliequivalent per gram range, but this value depends on the substances added to the carbon during the activation process.

Similar to ion exchange resins with basic and acidic functional groups, respectively, H- carbons produce a basic pH in solution pH while L- carbons yield an acidic solution pH.(6) Since no acid or base can be extracted from the solution after contact with the carbon, the conclusion is made that surface structures are responsible for this phenomenon. Electrokinetic studies have indicated that H- carbons exhibit a positive surface potential, as opposed to a negative surface potential for L- carbons. However, unless care is taken to cool H- carbons in an inert atmosphere after activation, formation of structures which change the potential from positive to negative does occur. The presence of inorganic constituents at the surface may also affect the potential to the point of reversing its sign from that which might be expected on the basis of the activation temperature.

A negative potential for L- carbons is consistent with the presence of surface acids, while the existence of a positive potential for H- carbons requires further consideration. Garten and Weiss(6,28), using various techniques for the study of L-carbons, have concluded that surface acids responsible for the sorption of alkali from aqueous solution consist of at least three fundamental types: 1. phenol; 2. n-lactone; and, 3. f-lactone - the type present in fluorescein and phthalein dye-stuffs.(28) The relative proportions of these three groups vary with the method of preparation of the active carbon.(6)

In determining the total number of acid groups present on L- carbons by base titrations, Garten and Weiss noted that the titration curves closely resembled the type obtained for weak acids, and were comparable to that for titration of a phenolic functional group ion-exchange resin.(28) These observations point to the possibility of phenolic surface structures, as illustrated in Figure 2. By way of additional evidence, a certain proportion of the acidic groups have been found to methylate with diazomethane, but the methoxyl group thus introduced resists hydrolysis when treated with boiling, dilute acid. This behavior is characteristic of the phenolic structure.(28) Conversely, a portion of the total number of acidic groups have been found to resist methylation with diazomethane, while supplementary infra-red spectroscopy studies have produced data consistent with the postulation that these groups are of the n-lactone type given in Figure 3, an absorption band having been found at 1,710 cm^{-1}.(28)

A third fraction of the acidic groups on L- carbons has been found to methylate with diazomethane, but with the methoxyl group thus formed being hydrolyzable in dilute boiling acid.(28) Carbon compounds which have phenolic groups in association with lactone groups, as in fluorescein or phthalein dyestuffs, act similarly. Figure 4 gives illustration of the structure of such lactones, called _f_-lactones.(28) The infra-red data referred to previously has also revealed an absorption peak at 1,750 cm^{-1}, consistent with the presence of _f_-lactones.

While simple base titration has been used rather extensively for measurement of the total number of acid groups present on carbon, some questions have been raised as to the quantitativeness of this procedure. For example, Studebaker(29), using sodium aminoethoxide in ethylene diamine as a titrant and comparing his results with those obtained by base titration, has found that base titration determines only about 68% of the total acidity as measured by the aminoethoxide titration.

Quinone groups are also known to be present on the surface of active carbon.(6,29,30) An H- carbon cooled in nitrogen gas after activation does not sorb base, but reduction of the H- carbon with sodium borohydride develops base sorbing properties.(29,30) This observation can be explained in terms of quinone reduction to hydroquinone.(29,30) Hallum and Drushel(31) also have found polarographic evidence for quinones. Reduced quinones, or hydroquinonces, might be expected to behave as phenols when treated with diazomethane, and thus would be included in the phenolic fraction given by the method of analysis used by Garten and Weiss.

It is quite interesting to note that although a carbon activated at a temperature of 800 - 1,000°C will sorb acid, evacuation at the temperature of activation followed by cooling in an inert atmosphere will so affect the carbon that it will not sorb acid from a deaerated solution until oxygen is admitted.(13) Indeed, an exponental relationship exists between the acid sorbed and oxygen partial pressure for the range 0-20 mm-Hg.(6) It has been found by Kolthoff that hydrogen peroxide is released by carbon to a solution from which acid is adsorbed.(30) Garten and Weiss(13), on the basis of this phenomenon, propose the presence of chromene (benzopyran) groups on the H- carbon surface. As illustrated in Figure 5, this structure contains an activated $>CH_2$ or $>CHR$ group which can react with a strong acid and oxygen.(33) There is much difficulty in establishing the stoichiometry of this reaction, however, because active carbon also catalyses the breakdown of the hydrogen peroxide.(13)

The carbonium ion formed by acid reaction with the chromene group, as shown in Figure 5, will hydrolyze readily in water to form the chromenol group illustrated in Figure 6, a weakly basic group having a dissociation constant of 10^{-11}.(34) The fact that the carbonium ion tends to associate so strongly with a negative ion could account for the fact that sorbed acid is very difficult to wash from carbon.(13)

In addition to the evidence for chemisorption and the chromene groups, there is also strong evidence that some physical sorption of acid takes place.(6) Garten and Weiss(6) have shown that a portion of the sorbed acid on an acid-saturated carbon can be displaced by strongly adsorbed organic molecules. The assumption is made that the physically sorbed acid can be displaced and the chemisorbed acid can not. By this means an approximation can be made of the number of chromene groups present on the carbon surface. The relative proportion of the quantity of acid physically sorbed to that chemically sorbed again depends on the method of preparation, especially the length of time the carbon is activated.(6)

Summary

An attempt has been made to develop an elementary conceptual model for description of the nature and behavior of the surface of active carbon. The purpose of this initial model is to set forth some of the more significant interfacial factors and mechanisms to be considered in interpretation of sorption phenomena associated with active carbon in aqueous solutions, and to provide a basis for further research aimed at more thorough delineation of sorption processes. In the development of this model it has been necessary to examine the basic structural unit of active carbon, the microcrystallite, and those factors which affect its formation during the manufacturing process. Production variables such as raw material, temperatures of carbonization and activation, additives used for catalysis of carbonization and activation or for the development of specific sorptive properties all seem important in establishing the course of formation of the microcrystallite, and thus the active carbon surface.

Pore surfaces of active carbon appear to consist principally of either the planar or the edge surfaces of the microcrystallite. The planar surfaces are relatively homogeneous, but the edge surfaces are heterogeneous, quite probably covered with oxygen- and hydrogen-containing functional groups. Some of the oxygen complexes appear to be highly reactive with certain inorganic species in aqueous solution, particularly acids and bases. This interaction can be especially significant for active carbons having appreciable quantities of surface oxygen, since it probably results in changes in the nature of the pore surface.

Ash content, which is appreciable for most commercial carbons, might also be expected to markedly affect the nature of the active carbon surface if the inorganic species are distributed over the internal surface of the pores. If the ash is localized in specific vacancies rather than distributed over the pore interior, however, the sorptive properties are likely to be affected very little.

There is yet much to be learned concerning the nature and interfacial activity of active carbon surfaces before our knowledge of adsorption processes involving this material can in any way be considered complete. Hopefully the present discussion provides a start in this direction.

Acknowledgment

These studies have been supported, in part, by Research Grant WP-00706 from the Division of Water Supply and Pollution Control, United States Public Health Service.

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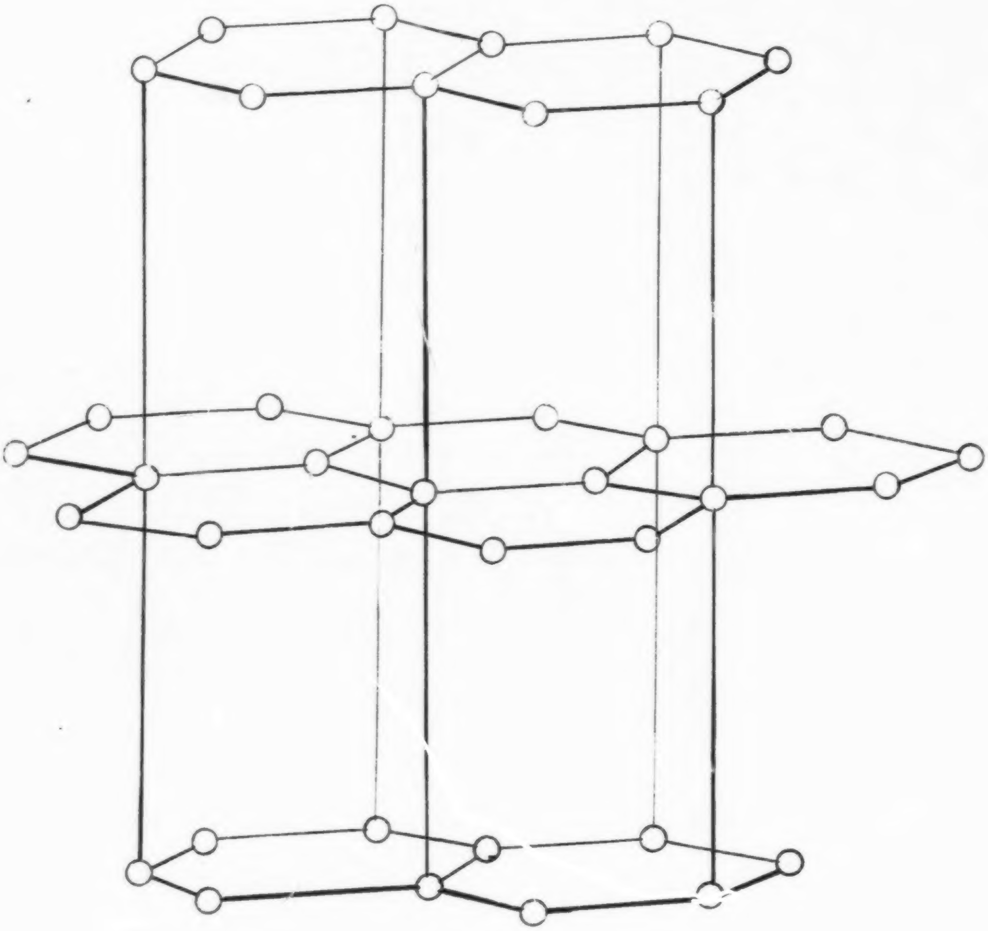

Figure 1. THE ARRANGEMENT OF CARBON ATOMS IN THE GRAPHITE CRYSTAL[12]

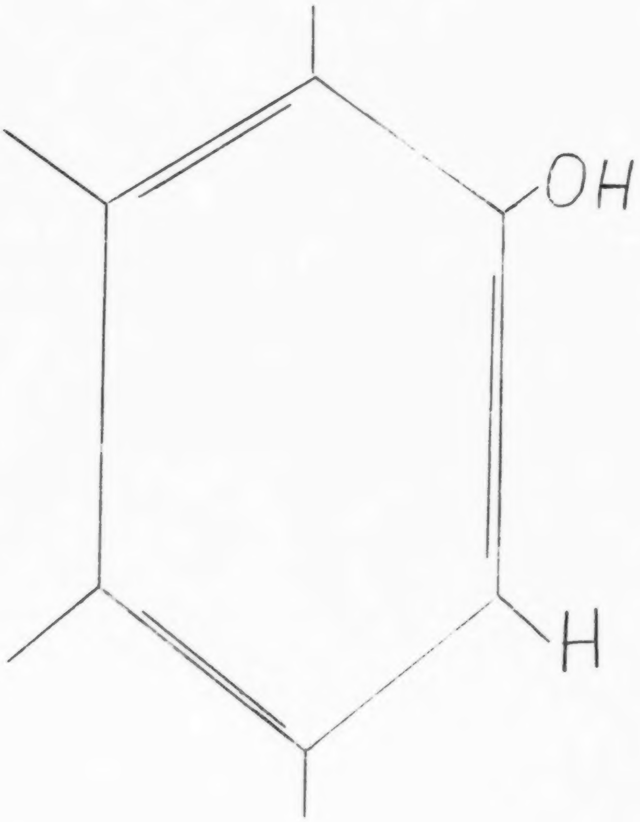

Figure 2. A PHENOLIC SURFACE STRUCTURE[6]

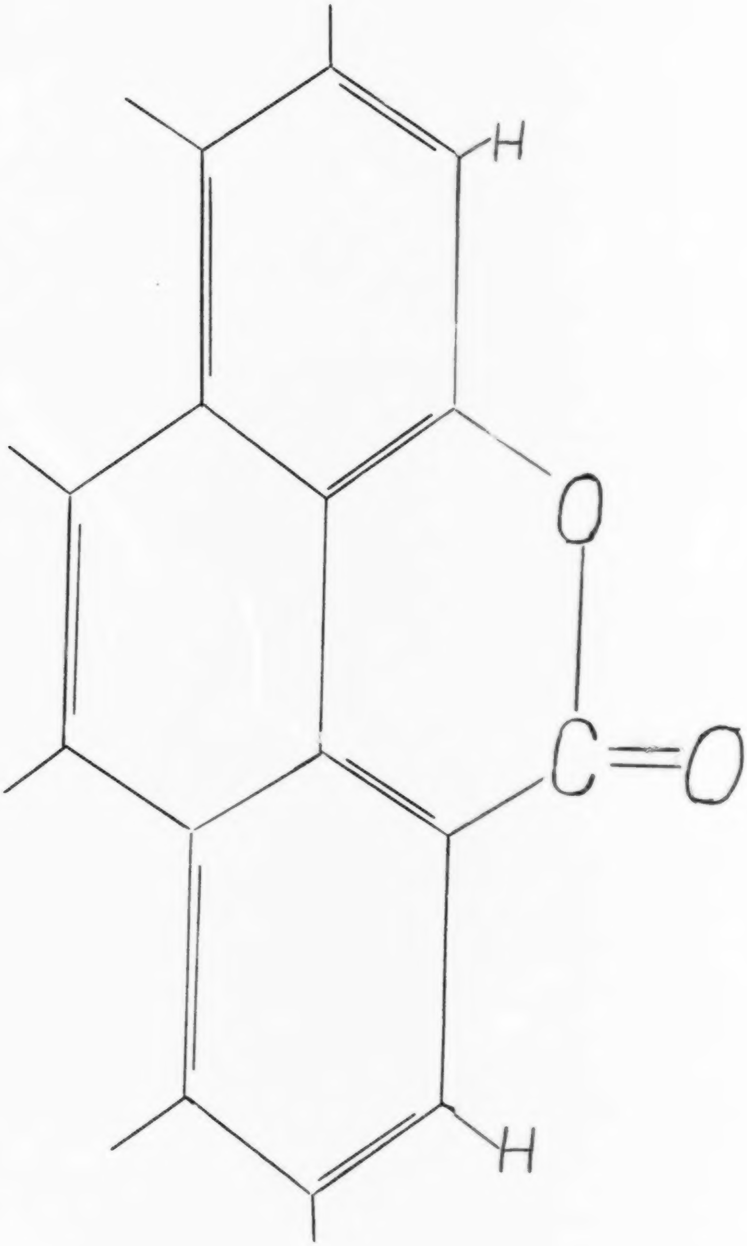

Figure 3. A n-LACTONE SURFACE STRUCTURE[6]

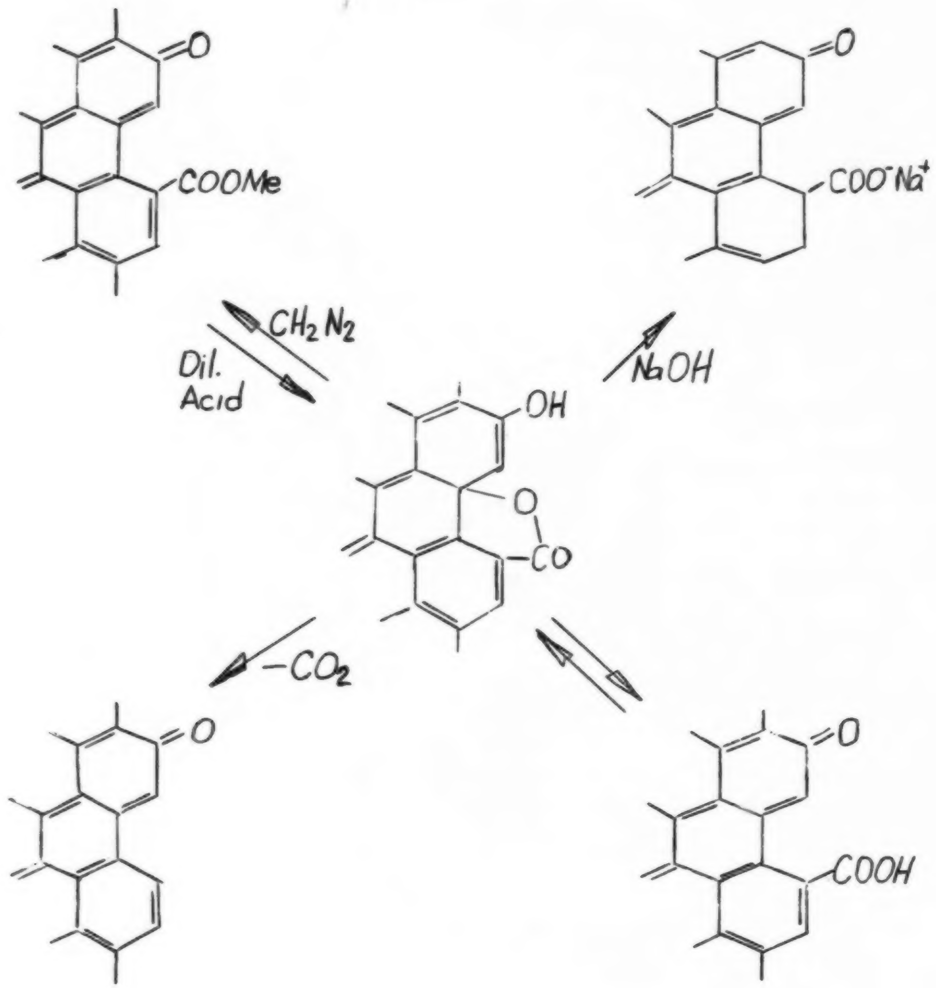
=O
COOMe
CH₂N₂
Dil. Acid
=O
COO⁻Na⁺
NaOH
OH
O
CO
−CO₂
=O
=O
COOH

Figure 4. SOME REACTIONS OF FLUORESCEIN-TYPE LACTONES[28]

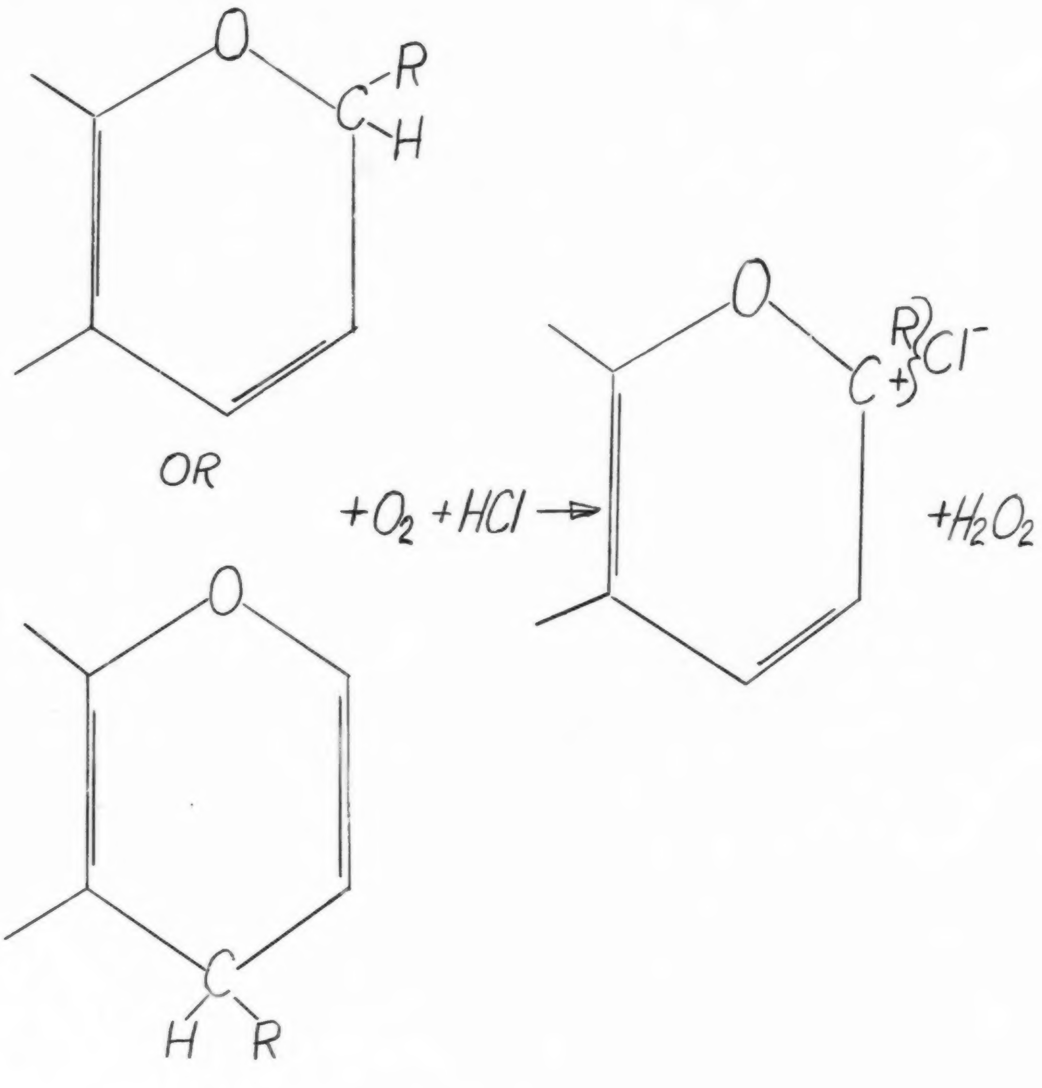
OR
+O2 +HCl
+H2O2
R
H
Cl⁻
O

Figure 5. THE CHROMENE-ACID REACTION[13]

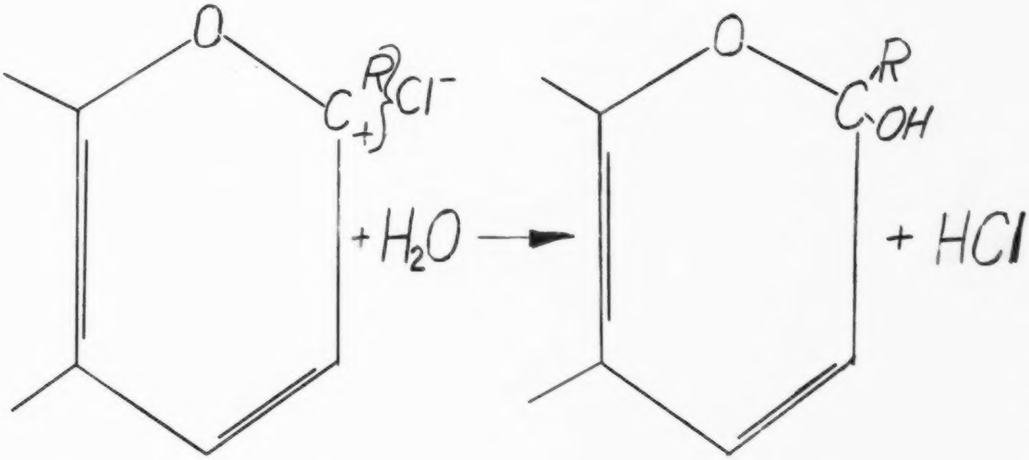
O
R
Cl⁻
C
+
+H₂O
O
R
C
OH
+ HCl

Figure 6. HYDROLYSIS OF THE CARBONIUM ION[13]